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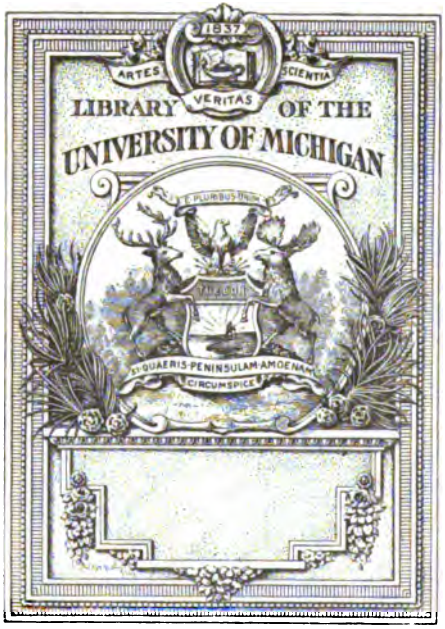

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TRANSACTIONS

OF THE

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VOLUME XIII

Containing Papers and Discussions Read at the Meeting Held at Trenton, N. J., Feb. 14th, 15th and 16th, 1911

This society is not, as an organization, responsible for the statements of facts or opinions expressed in these papers and discussions.

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WHITEHEAD, C. LOUIS, Box 153, Trenton, N. J.	President, Providential Tile Company.
WHITMER, J. D., CR.E., Zanesville, Ohio.	Am. Encaustic Tile Co.

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WHITTAKER, JOHN L., East Boston, Mass.	Superintendent, New England Pottery Company.
WILDER, THOMAS MILTON, Ravinia, Ill.	Proprietor, Wildwood Shop.
WILL, OTTO W., Perth Amboy, N. J.	Superintendent, Color Department, Roessler & Hasslacher Chemical Company.
WILLIAMS, ARTHUR E., 121 S. Fifth St., Monmouth, Ill.	Monmouth Brick & Tile Company.
WILLIAMS, IRA A., M.Sc., Ames, Iowa.	Associate Professor, Geology and Mining Engineering, Iowa State College.
WILLIAMS, WARREN STEPHEN, B.S., North Crystal Lake, Ill.	American Terra Cotta & Ceramic Company.
WIRT, HERBERT C., Burrage, Mass.	President, Wirt Manufacturing Company.
WORTH, S. HARRY, 706 Franklin Bank Building, Philadelphia, Pa.	President, Pennsylvania Feldspar Company.
YATES, ALFRED, Shawmut, Elk Co., Pa.	General Manager, Shawmut Paving Brick Company.
YOUNG, GEORGE F., Zanesville, Ohio.	Manager, Roseville Pottery Company.
YOUNG, SAMUEL ECCLES, C.E., 3451 California Ave., N. S., Pittsburg, Pa.	Aid, Bureau of Standards.
YOWELL, JOHN BENNETT, 1322 Center St., Little Rock, Ark.	Arkansas Brick & Manufacturing Company.
ZOPFI, ALBERT S., Toledo, Ohio.	Secretary and Treasurer, Buckeye Clay Pot Company.

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RULES OF THE SOCIETY.

I.
OBJECTS.

The objects of the American Ceramic Society are to promote the arts and sciences connected with ceramics by means of meetings for the reading and discussion of professional papers, the publication of professional literature, and for social intercourse.

II.
MEMBERSHIP.

The Society shall consist of Honorary Members, Active Members, Associate Members and Contributing Members.

Honorary Members must be persons of acknowledged professional eminence, whom the Society wishes to honor in recognition of their achievements in ceramic science or art. Their number shall at no time exceed two per cent. of the combined active and associate membership.

Active Members must be persons competent to fill responsible positions in ceramics. Only Associate Members shall be eligible to election as Active Members, and such election shall occur only in recognition of attainments in the field of ceramics, and interest in the Society, as evidenced by papers or discussions contributed to its meetings.

Associate Members must be persons interested in ceramics or allied arts.

Contributing Members must be persons, firms, or corporations who being interested in the Society make such financial contributions for its support as are prescribed in Section 3.

Honorary Members shall be nominated for election by at least five active members, and approved by the Board of Trustees. Their nomination shall be placed before the Society at an annual meeting, and to be elected they must receive the affirmative vote of at least 90 per cent. of those voting, by letter ballot, at the next succeeding annual meeting.

To be promoted to active membership, Associate Members must be nominated in writing by an Active Member, and must be seconded by not less than two other Active Members, and must be approved by the Board of Trustees. Their nomination shall be accompanied by a statement of their professional qualifications and a list of their publications, if any. Their nominations, when approved by the Board of Trustees, shall be placed before the Society at an annual meeting, and to be elected they must receive the affirmative vote of not less than 75 per cent. of those voting, by letter ballot, at the next succeeding annual meeting.

A candidate for Associate Membership must make application upon a form, prepared by the Board of Trustees, which shall contain a written statement of the age and professional experience of the candidate, and a pledge to conform to the laws, rules and requirements of the Society. Such applications must be endorsed by two Active Members of the Society as

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sponsors, and must be approved by the Board of Trustees. The Board may act by letter ballot upon such application at any time, after which an approved candidate may be enrolled on the proper list of the Society upon payment of the fees and dues prescribed in Section 3.

Contributing Members shall be nominated by an Active Member, and approved by the Board of Trustees, and may be enrolled on the proper list of the Society at any time upon payment of the dues prescribed in Section 3.

All Honorary Members, Active Members, Associate Members, and Contributing Members, shall be equally entitled to the privileges of membership, except that only Active Members shall be entitled to vote and hold office. The roster of each grade of membership shall be printed separately, in at least one publication issued by the Society annually. Any person may be expelled from any grade of the membership of the Society if charges signed by five or more active members are filed against him, and a majority of the Board of Trustees examines into said charges and sustains them. Such person, however, shall first be notified of the charges against him, and be given a reasonable time to appear before the Board of Trustees, or present a written defense, before final action is taken by the Board of Trustees.

III.
DUES.

Honorary Members shall be exempt from all fees or dues.

The initiation fee of Active Members shall be ten dollars, and if not paid within three months after the date of their election, the latter shall be null and void. The annual dues for Active Members shall be fixed by the Board of Trustees, and shall not exceed ten dollars.

The initiation fee of Associate Members shall be five dollars, and their annual dues shall be fixed by the Board of Trustees, but shall not exceed five dollars. The privileges of Associate Membership after election shall begin upon payment of the initiation fees, and dues for the first year.

Contributing Members shall pay no initiation fee into the Society. Their annual dues shall be fixed by the Board of Trustees, but shall not exceed twenty-five dollars. The privileges of membership shall begin upon payment of the annual dues.

Any Active Member or Associate Member in arrears for over one year may be suspended from membership by the Board of Trustees, until such arrears are paid, and in event of continued dereliction, may be dropped from the rolls. Active Members in arrears are not eligible to vote. The annual dues of Active and Associate Members are payable within three months succeeding date of annual meeting.

IV.
OFFICERS.

The affairs of the Society shall be managed by a Board of Trustees, consisting of a President, Vice-President, Secretary, Treasurer, and three

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Trustees, who shall be elected from the Active Members at the annual meeting, and hold office until their successors are elected and installed.

The President, Vice-President, Secretary and Treasurer shall be elected for one year, and the Trustees for three years; and no President, Vice-President, or Trustee shall be eligible for immediate re-election to the same office.

The duties of all officers shall be such as usually pertain to their offices, or may be delegated to them by the Board of Trustees or the Society; and the Board of Trustees may at its discretion require bonds to be furnished by the Treasurer.

Vacancies in any office shall be filled by appointment by the Board of Trustees, but the new incumbent shall not thereby be rendered ineligible to re-election at the next annual meeting to the same office. On the failure of any officer to execute his duties within a reasonable time, the Board of Trustees, after duly warning such officer, may declare the office vacant, and appoint a new incumbent.

A majority of the Board of Trustees shall constitute a quorum; but the Board of Trustees shall be permitted to carry on such business as it may desire by letter.

V.

ELECTIONS.

At the annual meeting, a Nominating Committee of five Active Members, not officers of the Society, shall be appointed, and this committee shall send the names of the nominees to the Secretary at least sixty days before the annual meeting who shall immediately forward the same to the Active Members. Any other five Active Members may act as a self-constituted Nominating Committee, and also present the names of any nominees to the Secretary, provided it is done at least thirty days before the annual meeting. The names of all nominees, provided their assent has been obtained, shall be placed on the ballot without distinction as to nomination by the regular or self-constituted Nominating Committee, and shall be mailed to every member, not in arrears, at least twenty days before the annual meeting. The ballot shall be enclosed in an inner blank envelope, and the outer envelope shall be endorsed by the voter, and mailed to the Secretary. The blank envelopes shall be opened by three scrutineers appointed by the President, who will report the result of the election at the last session of the annual meeting. A plurality of votes cast shall elect.

VI.

MEETINGS.

The annual meeting shall take place on the first Monday in February, or as soon thereafter as can be conveniently arranged, at such place as the Board of Trustees may decide, at which time a report shall be made by the Board of Trustees, Treasurer and scrutineers of election, and the accounts

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of the Treasurer shall be audited by a committee of three, appointed by the President. Ten Active Members shall constitute a quorum at any regular meeting, and a majority shall rule unless otherwise specified.

The order of business at the annual meeting shall be:

1. President's address.
2. Reading of minutes of last meeting.
3. Reports of the Board of Trustees and Treasurer.
4. Appointment of committees.
5. Old business.
6. New business.
7. Reading of papers.
8. Announcement of election of officers, Honorary and Active Members.
9. Installation of officers and new members.
10. Adjournment.

Other meetings may be held at such time and places during the year as the Board of Trustees may decide, but at least twenty days' notice shall be given of any meeting.

The President shall appoint at the annual meeting a committee of five, to be known as the Summer Meeting Committee, whose duty it shall be to arrange for a summer excursion meeting at some suitable point. The expenses of the Summer Meeting Committee in arranging the program of visits, and for printing, rooms and facilities for meetings, shall be borne by the Society.

VII.

PUBLICATIONS.

The Board of Trustees shall employ, at suitable compensation, an Active Member of the Society as Editor of its publications. The Editor, together with the Secretary and Treasurer, shall constitute a Publication Committee. The Publication Committee shall provide for the publication of an annual volume entitled "Transactions of the American Ceramic Society." This volume shall contain a list of the officers, a list of the members of the Society, classified into grades, a list of the ex-Presidents, the dates and location of meetings, the annual report of the Board of Trustees and Treasurer, the list of prices of the publications of the Society, the rules of the Society, and any other matter pertaining to the business administration of the Society that the Publication Committee may think proper. It shall also contain such of the papers and discussions thereon as the Publication Committee may consider desirable, and each volume shall contain a list of the papers and discussions and an index. The volume shall be six inches wide by nine inches long, and part of the issue shall be bound in paper covers and part in cloth binding. The quality of the paper, the kind of type, the illustrations, and all other mechanical details of the printing and publishing of the books of reprints shall be in the hands of the Publication Committee, subject to the control of the Board of Trustees.

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The acts and policies of the Publication Committee shall at all times be subject to the examination and approval of the Board of Trustees, but the Board shall be bound by contracts entered into by the Publication Committee in the name of the Society. The Publication Committee shall have full power and authority to decide what papers and discussions to publish, which discussions shall be germane to the subject matter, and in what order they shall be published, and in what manner and to what extent they shall be illustrated. In event that the Board of Trustees shall undertake the publication of some other matter or book than the Transactions, the Publication Committee shall act in the same capacity for that publication as in the publication of the annual volume of the Transactions.

One copy of the paper-bound edition of the Transactions shall be sent prepaid to each member of the Society not in arrears. Members desiring cloth-bound copies will be furnished them in place of the paper-bound copy at an increased cost for the binding. No member shall be furnished more than one copy of the Transactions free for any single year. Members cannot purchase extra copies of the Transactions at less than the current commercial rates. A member shall be permitted to purchase one complete file of the publications of the Society at less than the current commercial rate, the amount to be fixed by the Publication Committee and called the Member's rate.

The Secretary shall have the custody of all publications of the Society, shall keep them safely stored and insured, and shall sell these volumes to the public at prices which shall be fixed by the Publication Committee for each new volume as issued. The Publication Committee shall also, from time to time, fix the price of the old volumes remaining unsold, and shall have authority to refuse to sell the old volumes of the Transactions except in sets, at such time as the quantity remaining of any number becomes so small, as in their judgment to warrant such action.

The Editor shall request the author of each article appearing in the Transactions of the Society to fill out and sign, within a definite time limit, a blank form, specifying the number of reprints of said article, if any, which he desires. This form shall contain a table from which can be computed the approximate cost at which any reprints will be furnished. In event that the expense of furnishing the desired number of reprints is large, the Publication Committee may require the author to pay in advance for part or all of the cost involved before the publication of the reprints is begun. On receipt of such signed order within the time limit set, the Editor shall cause to have printed the desired number of copies. If the author makes no reply, or replies after the time limit has expired, then the Society will not be responsible for the publication of any reprints of the article in question, except at the usual market price for the printing of new matter.

No one shall have the right to demand the publication of an article independent of the discussion which accompanied it, and no one having

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taken part in a discussion upon an article shall be entitled to order reprints of the discussion separately and apart from the article itself.

The Society is not, as a body, responsible for the statements of facts or opinions expressed by individuals in its publications.

VIII.

PARLIAMENTARY STANDARD.

Roberts "Rules of Order" shall be the parliamentary standard on all points not covered by these rules.

IX.

AMENDMENTS.

To amend these rules, the amendment must be presented, in writing, at the annual meeting of the Society, and must be printed on the ballot for officers and sent out not less than twenty days in advance of the next annual meeting, and if the said letter ballot shows an affirmative vote of not less than two-thirds of the total vote cast, then the same shall be declared carried.

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PUBLICATIONS.

The following is a list of the volumes published by the Society and the prices at which they are for sale to the general public:

Description of volume.			Bound in paper.	Bound in cloth.
Vol. I.	1899,	110 pages	$ 4 00	$ 4 75
Vol. II.	1900,	278 pages	4 00	4 75
Vol. III.	1901,	238 pages	4 00	4 75
Vol. IV.	1902,	300 pages	4 00	4 75
Vol. V.	1903,	420 pages	5 00	5 75
Vol. VI.	1904,	278 pages	4 00	4 75
Vol. VII.	1905,	454 pages	4 00	4 75
Vol. VIII.	1906,	411 pages	4 00	4 75
Vol. IX.	1907,	808 pages	5 00	5 75
Vol. X.	1908,	582 pages	5 00	5 75
Vol. XI.	1909,	632 pages	5 50	6 25
Vol. XII.	1910,	882 pages	5 50	6 25
Vol. XIII.	1911,	— pages	5 50	6 25
Complete set			$59 50	$69 25

The Board of Trustees established in the beginning a differential between members of the Society and others, in the matter of prices to be paid for copies of the Proceedings. This differential has been changed from time to time as volumes have grown scarcer and sales increased. The present arrangement, which will stand until March 1, 1912, allows a straight discount of 40 per cent. to members in good standing. Members in arrears are not furnished copies of the volume for the current year, nor allowed the discount for the older publications. Members are also not permitted to purchase more than one full set of the publications at members' rates. The care and sale of the Publications has been transferred to the Publication Board, which reserves the right to change the discount from time to time on any one volume or on all, as may be necessary.

The number of copies of the earlier volumes is not large, and members are advised to procure full sets as soon as possible. The prices will never be less and will certainly raise as time goes on.

In addition to the above volumes of the Transactions, the Society has also published the following books, which will be sold *net* at the prices listed to the public and members alike:

The Collected Writings of Dr. Hermann August Seger, Volume I. Contains (*a*) Treatises of a General Scientific Nature. (*b*) Essays Relating to Brick and Terra Cotta, Earthenware and Stoneware, and Refractory Wares. Pages, 552. Bound in cloth..... $ 7 50

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The Collected Writings of Dr. Hermann August Seger, Volume II. (*b*) Essays on White Ware and Porcelain. (*c*) Travels, Letters and Polemics. (*d*) Uncompleted Works and Extracts from the Archives of the Royal Porcelain Factory. Pages, 605. Bound in cloth..... $ 7 50

A Biography of Clays and the Ceramic Arts, by Dr. John C. Branner, 1906, 451 pages. Bound in cloth. Contains 6027 titles of works on Ceramic subjects ..... $ 2 00

The above publications will be shipped at the consignee's expense, by express, to any address on receipt of the price. All checks or money orders should be made payable to The American Ceramic Society, and not to the Secretary or the Treasurer.

EDWARD ORTON, JR.,
Secretary.

Columbus, Ohio.

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ANNUAL REPORT OF THE BOARD OF TRUSTEES.

To the Members and Associates of the American Ceramic Society:

The Society has closed its twelfth year of active and successful work and is about to assemble for its thirteenth Convention. The following statements reflect its condition in all important respects as fully as possible.

VOLUME TWELVE.

This volume is our largest and most important to date. It contains 880 pages, and in spite of the fact that the paper used is dense and solid, and not heavier than need be, the book is larger than any of the volumes in which soft thick paper was used, excepting Volume IX. The limit of thickness and weight for convenient reading and shipping has been practically reached, and to avoid enlargement, more care and condensation in editing will probably be used hereafter.

FINANCIAL STATEMENT.

The financial statement of the Society is as follows:

Income.

Brought forward from preceding year			$ 73.86
From Dues and Initiation Fees:			
306 Associate dues for 1910 @ $4.00		$1,224.00	
10 Associate dues for 1909 @ 4.00		40.00	
1 Associate dues for 1909 @ 2.00		2.00	
4 Associate dues for 1911 @ 4.00		16.00	
58 Associate initiation fees 1910 @ 5.00		290.00	
3 Associate initiation fees 1911 @ 5.00		15.00	
1 Associate initiation fees 1909 @ 5.00		5.00	
52 Full Members dues for 1910 @ $5.00		260.00	
1 Full Members dues for 1909 @ 5.00		5.00	
2 Associates overpaid	$4.00	8.00	
1 Full Mem. overpaid	5.00	5.00	
3 Associates overpaid	0.50	1.50	
Foreign exchange		0.35	1,871.85
Book Binding Fund			203.35
From sale of Publications:			
Volume I	16		
Volume II	25		
Volume III	14		
Volume IV	13		
Volume V	14		

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Volume VI	15		
Volume VII	17		
Volume VIII	15		
Volume IX	24		
Volume X	22		
Volume XI	30		
Volume XII	53	1,073.48	
Branner Bibliography (6 free)	7	13.74	
Segers Collected Writings Vol. I	4		
Segers Collected Writings Vol. II	5	67.50	1,154.72
From sale of Reprints			226.75
Refund			17.03
Total cash received			$ 3,547.56

Disbursements.

Cost of Publishing Volume XII:		
Stenographic Report	$ 159.40	
Illustrations, Drawing and Engravings	311.10	
Printing, Binding and Casing	1,306.73	
Editor's salary	600.00	$2,377.23
Cost of Seger's Collected Writings		49.58
Cost of running Secretary's office:		
Salary of accountant	300.00	
Postage, Stationery and Supplies	177.91	
Express on Transactions	88.19	
Convention Expense	76.61	
Insurance on Transactions	10.00	
Corporation fees	1.00	
Binding extra sets of Transactions	66.45	720.16
Cost of Reprints		226.75
Refunds		13.00
Check returned on account of no funds		9.00
Total amount expended		3,395.72
Cash in Bank		151.84
Total		3,547.56
Outstanding accounts:		
Dues and Fees	99.30	
Transactions	23.60	
Branner Bibliography	2.00	
Seger's Collected Writings	7.50	132.40

Cost of Volume XII $2,377.23 + 599, $3.96 each.

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The statement shows the situation far better than was expected during the last few months. During the fall the condition of our treasury became somewhat alarming. There was a large list of members in arrears, and sales for some time had been going slow, and the printer's bill coming at this time made it seem questionable whether the Society could get through the year without incurring a deficit. Vigorous work on the part of the Secretary for a couple of months brought in a very considerable proportion of the outstanding credits. The number of members now in arrears is somewhat less than usual at the end of the year, and the accounts payable are also collected up to a small amount. The result is that the Society has been able to come through the year handsomely, with cash in bank and an outstanding account substantially the same as that of a year ago.

There has been an actual increase in the income of the Society amounting to $710.74. This increase has been derived chiefly from three sources:

First.—A higher price has been charged for the old volumes of the Society, the stock of which has become constantly more depleted.

Second.—Our sales have been larger than ever before, the amount of the increase being nearly $400.

Third.—There has been an increase of about $250 in the amount of money received from dues, owing to our constant increase in membership.

It has been possible, owing to the various sources of increase, for the Society to pass through the year of increased business and increased expense without any appreciable change in its financial status of a year ago.

It must not be assumed, however, that the above condition is a healthy or satisfactory one. It means that these results have been attained without the Society paying in full for the service which it receives. This is true both as to the cost of the office administration and the cost of the Editor, neither one of which have ever been put upon a strictly commercial basis. With the sources of revenue hitherto available this service has been given either free or at small rates of compensation. But under the new provisions of the Constitution, which comes before the Society for adoption at this time, there are new sources of revenue proposed which will make it possible for the Society to work upon a somewhat different basis.

The contributing membership scheme, which has been before the Society for three years past, if adopted at this time, will open a very considerable source of income. Also the time has now been reached when the dues of the Society can be properly raised, as the output of literature has now reached a point where the price charged is really a low one for the matter furnished. It seems therefore that if the Society desires to take a step forward in its policy that the means are now close at hand.

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PUBLICATIONS.

The annual inventory of the publications is as follows:

	Remaining on hand Feb 1st, 1910.	Received since.	Disposed of since by sale or otherwise.	In stock according to books.	In stock by actual inventory.
Volume I	207	...	17	190	190
Volume II	192	...	26	166	166
Volume III	202	...	14	188	188
Volume IV	172	...	13	159	159
Volume V	142	...	14	128	128
Volume VI	173	...	15	158	158
Volume VII	173	...	17	156	156
Volume VIII	164	...	15	149	149
Volume IX	137	...	24	113	113
Volume X	167	...	22	145	144–1
Volume XI	205	...	40	165	165
Volume XII	...	599	432	167	167
Branner Bib	839	...	13	826	825–1
Totals	2,773	599	662	2,710	2,708

Shortage, unaccounted for —2.

The change in the status of the publications is very similar to what it has been heretofore. There is a small shrinkage in the total quantity of literature on hand; that is, the volumes brought in from the new edition of Volume XII have not quite replaced those by loss from sales of the various other volumes during the year. The quantity of volumes remaining in stock of the older issue is now well below 200, and in some instances pretty close to 100 copies. The price for these volumes have been increased during the last year, so that the difference between the members' rate and the rate to libraries and book-dealers and the rate to other casual purchasers is becoming less different than in former years. There still remains a considerable advantage to the members in purchasing our literature. Prices being figured on the basis of 100 per cent. for the casual purchaser, libraries and book-dealers can buy at about 80 per cent., and members at 65–70 per cent. This is sufficient to make it well worth while for those who are interested in our literature to take out associate membership, and pay their dues and fees in order to get the concession in price of the literature itself. Until the number of copies of the old volumes becomes reduced below 50, it would seem advisable to maintain the present situation. There will come a time,

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however, when the sale of the older volumes should be prohibited except in complete sets, and even then at a somewhat advanced rate.

The books are preserved and insured as in former years, and the total valuation of them at former rates is slightly above $6,000.

GROWTH IN MEMBERSHIP.

The year has been a good one. Our rolls stand as follows:

Brought forward from February 1, 1910:		
Honorary Members	2	2
Full Members, resident	51	
Full Members, foreign	3	54
Associate Members, resident	251	
Associate Members, foreign	33	284
Total		340
Accessions during the year:		
By election to full membership	0	
By election to full membership, foreign	0	
By election to associate	44	
By election to associate, foreign	3	
Elected at 1911 meeting as of the year 1910	10	57
Losses during the year:		
By resignation, associates	13	
By not knowing present address	2	
By death, A. M. Maddock	1	16
Brought forward February 1, 1911:		
Honorary Members	2	2
Full Members, resident	51	
Full Members, foreign	3	54
Associate Members, resident	292	
Associate Members, foreign	33	325
Total		381

The condition of our membership is seen to be excellent. The number of full members has not increased, owing to the postponement of the election until this meeting. It is probable that a very considerable increase in full membership will result from this election, and thus the apparent lack of change in this particular will be eliminated. Further, the constitutional changes which are proposed in reference to the mode of election of full members may possibly result in some change in this direction.

A card catalog has been prepared during the last year containing—*First*, a complete roster of the Society, edited from day to day according to the changes of address.

Second, and analysis of the volumes of the Transactions published, showing the title of each article and its page number. The total number of articles thus far published is 346.

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Third, an author's index showing the productions of each member of the Society who has yielded anything to our program. A subject index arranged in the same general manner is now in process of construction. The indices are all unquestionably valuable in the administration of the Society's affairs, and for the use of the Board of Trustees in Council meetings.

BUREAU OF MINES.

The political work done by the American Ceramic Society for some years past in behalf of the creation of a federal bureau of mines has at last borne fruit. Congress passed the necessary legislation for this bureau at its session closing June 25, 1910. The appropriation given to the new bureau was a somewhat liberal one, and has enabled it to take up its duties with vigor and zest. A disagreement, however, arose in the course of the legislation resulting in the partition of the work formerly carried on by the Technologic branch of the United States Geological Survey, by which the testing of structural materials was transferred to the supervision of the Bureau of Standards, instead of the Bureau of Mines.

Under this legislation the Bureau of Standards has taken charge of the clay products laboratory created by the Technologic Branch of the U. S. Geological Survey at Pittsburg, while the balance of the plant has passed into the control of the Bureau of Mines.

The interest of the Ceramic Society in this matter is purely that of getting the research work on ceramic problems carried through, and it is, of course, immaterial to it as an organization which branch of the federal service shall be intrusted with the execution of this work. The high quality of the research work done by the Bureau of Standards in other fields and the retention by the Bureau of the ceramic investigators which this Society was largely influential in bringing together in the earlier organization at Pittsburg, seem an excellent guarantee that the interests of this Society in the matter will be conserved. At the same time it is not improbable that the Bureau of Mines will be able to take up in due time the investigation of problems relating to the occurrence and winning of clays and the preparation of the clays for the market as raw materials, which will scarcely fall under the terms of the act relating to structural materials. It is therefore possible that this division of the field may result finally in an increase of the work in which the Ceramic Society is interested.

The continued interest of the members of the American Ceramic Society in both of these government bureaus and our sympathetic and effective coöperation with both of them in making them acquainted with our problems and needs is as necessary as at any time in the past.

SUMMER MEETING.

The summer meeting at Akron, Ohio, passed off successfully. The committee prepared an elaborate itinerary and the number attending the meeting, though not large, was sufficient to insure a profitable and enjoyable

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time. The general plan of definitely deciding on a place for a summer meeting and appointing a committee in advance has thus proven of value.

REVISION OF RULES.

The revision of the rules by the committee appointed for that purpose has been carried through, and the text of the proposed revision has been placed before the members in circular form, and action upon the same will be expected at this meeting. The proposed changes are mostly designed to incorporate into our rules provisions for the same procedure we have had in the past, for the Society has been following a closely uniform procedure for some years past, without carrying this procedure into its Constitution. The most important changes are those relating to the Publication Committee, the creation of a contributing membership, and provisions for the increase of dues.

THE MEETING PLACE.

For the first time, the Society has met at a point separate from the annual meeting of the National Brick Manufacturers' Association. During the week just closed the latter organization has held a very successful and enjoyable convention at Louisville, Ky. The present occasion is the best evidence that the American Ceramic Society will hold an equally profitable and prosperous meeting here at Trenton. It cannot be gainsaid, however, that there are members of both organizations who are reluctantly compelled to choose between them by reason of the present arrangements, and in general the best interests of both will be met by selecting a joint meeting place. It is also possible that the needs of the two organizations will occasionally require that they select different points, as the size of the attendance will make it impossible for the larger organization to go to many places that are of great interest to the American Ceramic Society and *vice versa*.

It is the earnest hope of the Board of Trustees that it will be possible to schedule a joint meeting with the N. B. M. A., for the ensuing year, 1912, and that meetings at different points shall not occur oftener than in alternate years, if that often.

In this connection the question of the date of meeting is to be seriously considered. A considerable proportion of our membership is attached to the various ceramic schools, and these members are necessarily somewhat bound by the school schedule. The fact that the close of the first semester and the opening of the second semester of nearly all the schools which maintain ceramic departments occurs in either the first or second week in February makes it a matter of very grave importance to this organization to secure some change in the meeting date. Postponement to the middle of February will in most cases probably avoid the critical weeks of the university year. It is hoped that the coöperation of N. B. M. A. can be secured on the question of date as well as location.

Very respectfully submitted,

Board of Trustees,

EDWARD ORTON, JR.,

Secretary.

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TREASURER'S REPORT.

RECEIPTS.

Balance from last report			$ 61.66
Total receipts per bank book and deposit slips attached		$3,485.90	
Less check to a member	5.00		
Less check entered twice	9.00	14.00	3,471.90
			3,533.56

EXPENDITURES.

Vouchers attached		3,346.33	
Less voucher returned also attached	5.00		
Less check returned unpaid in hands of Secretary	9.00	14.00	3,332.33

Vouchers issued but not presented for payment:			
Hann & Adair		35.26	
Edward Orton, Jr		5.00	
American Express Co		9.13	49.39
Bank balance			151.84
			3,533.56

ELLIS LOVEJOY, *Treasurer*,
Audited by STANLEY G. BURT,
ERNEST E. MAYER,
ROSS C. PURDY.

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IN MEMORIAM.

HARRISON EVERETT ASHLEY.

In the death of Harrison Everett Ashley the American Ceramic Society suffered a heavy loss. From the beginning of his work in the field of ceramics to the end, he was closely associated with our organization. He was at all times an enthusiastic supporter of its principles, and most loyal in its support. At the time of his death he was a member of the Board of Trustees, an office which he filled with zealous regard for the welfare of the Society.

Harrison Everett Ashley was born at New Bedford, Mass., August 2, 1876, the son of A. Davis and Caroline Morse Ashley. His early and secondary education he obtained in the public and high schools of New Bedford, and his collegiate training at the Massachusetts Institute of Technology. From this institution he was graduated in 1900 with the degree of S.B. in Chemical Engineering. During his college course Ashley specialized in metallurgy and consequently took up the technology of foundry metal and steel after leaving the institution. He held several positions in steel plants and foundries but meanwhile became exceedingly interested in silicates with special reference to slags and clays. Upon consulting with Prof. Orton and attending the Zanesville summer meeting of the Society he entered the employ of the Homer-Laughlin China Co., at East Liverpool, Ohio. He soon realized the advantage of securing special training along these lines and for this reason entered the Ohio State University in 1908 to take a special course of six months under Prof. Orton. Here his extraordinary research abilities were soon recognized and he was honored by the election to Sigma Xi, an honorary Society.

Upon his return to East Liverpool he was placed in charge of the kiln work and, later, of all the raw materials. When the great pottery plant at Newell, W. Virginia, was completed, the Homer-Laughlin Co. transferred him to the latter place where he tested all the materials used and had charge of the purchasing department of this large concern. On July 3, 1906, he was married to Miss Eva Susan Greenamyer, of Leetonia, Ohio, a step resulting in a union ideal in its happiness.

In 1908 Ashley received the appointment as assistant ceramic chemist with the Technologic Branch of the U. S. Geological Survey, and in 1910, upon the transfer of the work to the Bureau of Standards, he was promoted to be associate chemist. In this field he was thoroughly happy and worked unceasingly. He was at once struck with the importance of colloidal chemistry as applied to clays and proceeded to study the raw materials from this standpoint. He was successful in developing new lines of thought which he applied not only to clays but to lime hydrate, metallurgical slimes and other substances.

Mr. Ashley was a liberal contributor to technical literature and he has written articles and papers upon the following subjects: "The Study of Tellurium Alloys;" "The Use of the Triaxial Diagram in the Study of

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Slags;" "A Suggested Method of Studying the Gas Engine Cycle by Means of a Logarithmic Triaxial Diagram;" "The Production of Lustre Effects on Glass;" "The Effect of Various Lime Compounds upon a White Ware Body;" "The Diagrammatic Study of Glazes as Regards Their Crazing and Shivering Limits;" "The Testing of Pottery Materials;" "A Testing Method for Pottery Plaster;" "The Colloidal Content of Clays;" "The Control of Colloids in Clay;" "The Precipitation of Metallurgical Slimes;" and a Number of other papers. About a week before his death he completed a large bulletin dealing with the subject of the control of colloids which will appear as a publication of the Bureau of Standards.

Mr. Ashley underwent an operation for mastoid abscess several months after the Pittsburg meeting of the Society in 1910 and apparently was recovering satisfactorily. At the Mid-West Convention in Chicago, January, 1911, he appeared to be as well as usual but soon after his return was suddenly seized again by the treacherous disease which made necessary two operations. Meningitis developed and on February 4, 1911, Mr. Ashley departed from our midst. The funeral occurred on February 6th, at Pittsburg, and his body was taken to New Bedford.

Harrison Everett Ashley is in need of no eulogy. His character expressing itself constantly in purity of purpose, unselfishness and love of service, patience and kindness, he stands before us as a lofty example of manhood. His devotion to truth was an inspiration to all who knew him. To know him was to love him. His companionship was a delight and his views on the broad question of life were those of a generous and hopeful heart and of a sincere Christian.

Mr. Ashley is mourned by his widow, two young children, his parents and brothers. His death brought grief to his associates in the Pittsburg laboratories and to his friends of the American Ceramic Society.

His memory both as the able scientist and as the good man and loyal friend will continue to live with us.

ARCHIBALD MIDDLETON MADDOCK.

It is with feelings of profound sorrow that the officers and members of this Society record the death of one of its most honored Associate Members, Mr. Archibald Middleton Maddock, who died at his home in Trenton, New Jersey, on Friday, March 25, 1910, in the fifty-fourth year of his age.

His life's work was in the field of ceramics and the development of sanitary products, in which sphere he had gained not only eminent success but the admiration and respect of all who knew him. Being modest and unassuming, and always having a kind word and assisting hand, he had acquired a very large circle of friends and admirers.

In addition to his work in ceramic lines, he was a member of the Board of Directors of the Mechanics National Bank, of the Trenton Savings Fund Society, and of the Trenton School of Industrial Arts, and was Vice-President of the Board of Managers of the McKinley Memorial Hospital.

The American Ceramic Society desires to express to the family their sympathy in their loss, and to place upon record in a public way their appreciation of him as a ceramist and a man.

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PAPERS AND DISCUSSIONS.

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A REVIEW OF THE THEORIES OF THE ORIGIN OF WHITE RESIDUAL KAOLINS.

By HEINRICH RIES, Ithaca, N. Y.

In selecting a subject for my presidential address, it seemed desirable to take up some problem in the geology of clays that had a practical as well as a scientific bearing. I will, therefore, review the theories of the origin of the white residual clays, usually called kaolins, and point out the arguments for and against each.

For several centuries it has been known to geologists that the decomposition of feldspathic rocks, both igneous and metamorphic, has given rise to deposits of residual clays which, in many cases, are of white color. But, while the type of clay and character of the parent rock have long been recognized, there has been a wide difference of opinion regarding the exact mode of origin of the residual material derived from these two classes of rocks.[1]

The theories advanced to explain the formation of kaolin from feldspathic rocks are: (*a*) simple weathering, (*b*) post-volcanic emanations, (*c*) ascending spring waters containing carbon dioxide, (*d*) waters draining from swamps or peat bogs, (*e*) sulphuric acid solutions, (*f*) by the alteration of sericite.

KAOLINIZATION BY WEATHERING.

The oldest and most widely accepted theory of the origin of kaolin assumes that it has been formed by the weathering of rocks, a view that was expressed as early as 1791 by Werner.[2]

According to this theory, the kaolin is supposed to have been formed from feldspathic rocks by the ordinary weathering processes, *i. e.*, mechanical disintegration due to temperature changes, frost, and other physical agents, accompanied or followed by the decomposition of some of

[1] The occurrence of kaolin in limestones and sandstones is not here considered.

[2] Neue Theorie der Entstehung der Erzgänge, p. 130.

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the mineral grains, such as the feldspar, eventually transforming the whole into a white powdery mass. This powdery mass, known as kaolin, is made up wholly or in part of kaolinite or possibly some other hydrous aluminum silicate derived from the feldspar.[1]

Decomposition of the Feldspar.—The chemical changes involved in the transformation of the feldspar are as follows:

	SiO_2	Al_2O_3	K_2O	H_2O	Per cent of original
(1) Orthoclase	64.86	18.29	16.85	.....	100.00
Lost.....	43.24	.....	16.85	.....	60.09
Taken up....	.....	.....	.....	6.45	6.45
Kaolinite....	21.62	18.29	.....	6.45	46.36

	SiO_2	Al_2O_3	Na_2O	H_2O	Per cent of original
(2) Albite	68.81	19.40	11.79	.....	100.00
Lost.....	45.87	.....	11.79	.....	57.66
Taken up ...	.....	.....	.....	6.85	6.85
Kaolinite ...	22.94	19.40	.....	6.85	49.19

	SiO_2	Al_2O_3	CaO	H_2O	Per cent of original
(3) Anorthite...	43.30	36.63	20.07	.....	100.00
Lost	.....	.....	20.07	.....	20.07
Taken up ...	.....	.....	.....	12.92	12.92
Kaolinite ...	43.30	36.63	.....	12.92	92.85

The above indicates that orthoclase and albite lose two-thirds of the silica and all of the alkalies. Altogether, over half of the feldspathic constituents are lost in the

[1] For a more detailed statement see Ries, "Clay, Occurrence, Properties and Uses," 1908.

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decomposition, while anorthite loses only the lime. This proportional loss and gain may be expressed as follows:

Orthoclase.... $2Si_3O_8\,Alk - 4SiO_2 - K_2O + 2H_2O = Si_2O_9Al_2H_4$.
Albite..... $2Si_3O_8AlNa - 4SiO_2 - Na_2O + 2H_2O = Si_2O_9Al_2H_4$.
Anorthite..... $Si_2O_8Al_2Ca - CaO + 2H_2O = Si_2O_9Al_2H_4$.

Decomposition of the Micas.—Muscovite appears to be but little affected, while biotite or other ferromagnesian silicates, if present, may decay more or less rapidly.

Depth at which Weathering is Effective.—Decomposition by weathering begins normally at the surface, and extends downward, resulting in a gradual transition from the fully formed clay at the surface to the parent rock below. The depth to which the rock will be decomposed depends, naturally, upon the distance to which the weathering agents can penetrate, and this may vary in different parts of the rock, as in those portions which were abundantly jointed, the weathering agents could force their way much deeper. Moreover, since weathering agents are in some instances known to be effective at great depths, there is, obviously, a strong possibility that residual kaolins may exhibit a great vertical extent.

The Effect of Fissures.—The effect of fissures in facilitating the entrance of water was emphasized by Cohen and Deeke,[1] who thought that kaolinization first took place in and proceeded from the fissure systems which permitted the entrance of water.

Kaolinization is not Confined to Certain Kinds of Granite.—Delesse,[2] Andre,[3] and Laube[4] thought that kaolinization took place only in certain kinds of granite, a view now known to be incorrect.

The Effect of CO_2 Content of Percolating Waters.—It has usually been supposed that the decomposition of sili-

[1] Ueber das krystalline Grungebirge der Insel Bornholm, Jahresber. geol. Ges. Greifswald, 1889, IV.

[2] Ueber die Gegenwert von chemisch gebundenem Wasser in den Feldspath gesteinen, Ibid.. VI. p. 393.

[3] Studien über die Verwitterung des Granite, 1866.

[4] Geologische excursionen im bohmischen Thermalgebiet, Leipzig, 1884.

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cates in the rock, such as feldspar, is caused chiefly by the dissolved carbon dioxide often present in the percolating waters. This view was advanced by Forchammer as early as 1835[1] and also by later writers,[2] but as pointed out by Cameron and Bell,[3] this may be doubtful, in view of the fact that many minerals found in rocks are known to be soluble in water alone, although their solution may take place but slowly.

The water, moreover, is believed to react with or hydrolyze the minerals, as is shown by the fact that, after treating the powdered minerals with water free from dissolved carbon dioxide, an alkaline reaction can be obtained with phenolphthalein.

Difference in Rate of Solubility of the Different Minerals.—The rate of solubility varies with the different minerals, the magnesium-bearing micas being more soluble than muscovite, while the order of solubility of the feldspar is albite, oligoclase and orthoclase.[4] Clarke[5] found that muscovite, lepidolite, phlogopite, orthoclase, oligoclase, albite, leucite, nephelite, etc., were soluble in water, giving an alkaline reaction.

Decomposition of Orthoclase by Hydrolysis.—The action of water on orthoclase is assumed to be somewhat according to the following formula:[6]

$$KAlSi_3O_8 + HOH = KOH + HAlSi_3O_8.$$

The potassium hydrate thus formed may unite with carbon dioxide to form either a carbonate or bicarbonate of potash, or it is possible that it may unite with other acids forming salts more soluble in the hydrolyzed acid than the orthoclase.

The $HAlSi_3O_8$ formed is apparently unstable, and may

[1] Pogg. Ann., XXXV, p. 331, 1835.

[2] Rogers, Amer. Jour. Sci., V, p. 404, 1848; Bischof, Naturhist. Ver. Bonn, XII, p. 308, 1855; Daubree, Compt. rend., LXIV, p. 339, 1867; Miller, Tscherm., Mitth., 1877, p. 31; Laspeyres, Zeitschr. der Deutsch. Geol. Ges., 1864, p. 438.

[3] Bur. of Soils, Bull. 30, p. 16, 1905; also Cushman and Hubbard, Bull. 28, Office of Public Roads, Washington.

[4] Merrill, "Rocks, Rockweathering and Soils," p. 234, 1897.

[5] U. S. Geol. Surv., Bull. 167, p. 156, 1900.

[6] Cameron and Bell, Bur. of Soils, Bull. 30.

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lose some of its silica, resulting in the formation of kaolinite, pyrophyllite or diaspore, but in the weathering of feldspar the first of these appears to be more commonly produced.

Field Examples of Kaolinization by Weathering.— Occurrences of kaolins which clearly owe their origin to weathering processes are not uncommon, and a few examples may be noted, referring first to the American ones.

1. In Cecil County, Maryland, residual kaolins are found over an area of considerable size. These deposits are of great horizontal extent, but limited thickness, and, where tested to their full depth, are known to pass into the underlying granite, gneiss or schist, from which they have been derived by the simple process of weathering.[1]

2. At several localities in western North Carolina,[2] kaolin veins have been found in the metamorphic rocks, as for example in Harris kaolin mine near Webster. Here the white clay has been derived from a very coarse-grained pegmatite vein, consisting of quartz, feldspar, muscovite, and occasionally garnet. The kaolinization in this instance is clearly the result of decomposition of the feldspar, and extends to depths ranging from 80 to 125 feet.

3. Kaolin, formed by the weathering of feldspar, has been found in eastern Pennsylvania. That formerly worked at Brandywine Summit has been exhausted, and now the feldspar, from which it was derived, is being quarried.

4. Another clear case of the formation of kaolin by weathering is to be found in the so-called feldspar beds of the Cretaceous formation near Woodbridge, New Jersey.[3]

This material is a coarse arkose sand or gravel, consisting of a mixture of quartz, more or less decomposed feldspar, and pellets of white clay, together with small amounts of hornblend or pyroxene and undecomposed granitic pebbles. Some of the feldspar pebbles are an inch and a half in diameter, and all those which are unaltered show lustre on the cleavage planes.

[1] Ries, Md. Geol. Surv., VI, p. 455.
[2] Ries, N. C. Geol. Surv., Bull. 13, p. 60, 1897.
[3] Ries, N. J. Geol. Surv., VI, p. 177.

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The following analysis[1] shows the composition of the material in this deposit:

Sand	57.41
SiO_2	16.59
Al_2O_3	17.55
Fe_2O_3	0.54
TiO_2	0.90
Na_2O	0.21
Ign	6.30

5. Kaolin is found in the zone of oxidation of many ore bodies, and the fact that many writers note that it is strictly confined to the zone of oxidation proves that it is evidently due to weathering.[2] In some of these cases, however, its origin is explained as being due to the action of sulfuric acid on aluminous minerals, the acid being supplied by decomposing pyrite.

6. Turning now to foregin occurrences we find that Vogt[3] has described a kaolin deposit near Jösingsfjord at Ekersund-Söggendal, Norway, which he believes has resulted from labradorite, through the action of surface waters containing carbon dioxide. The transformation from rock to clay in this case is shown by the following analyses, No. I being the labradorite, No. II partly kaolinized rock, and No. III the kaolin.

	I	II	III
SiO_2	54.5	50.03	47.72
Al_2O_3	27.00	28.60	37.40
Fe_2O_3	2.5	1.62	1.59
CaO	9.0	4.21	0.23
MgO	1.0	2.95	0.11
Na_2O	5.0	1.00?	0.76
K_2O	1.0		0.44
H_2O	....	11.90	11.66
	100.00	100.31	99.91

[1] N. J. Geol. Surv. Rept. on Clays by G. H. Cook, 1878.

[2] See for example, Lindgren and Ransome, U. S. Geol. Surv., Prof. Paper 54, p. 129.

[3] Problems in the Geology of Ore Deposits, Amer. Inst. Min. Engrs., Trans., Feb., 1901. Also private communication.

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7. Wüst[1] has claimed an origin by weathering for the kaolins at Halle, Germany, and Winkel in his description of those found on the island of Bornholm, Denmark,[2] has shown that they grade downward into granite.

8. More recently Barnitzke[3] has shown that in the kaolin deposits of Meissen, Saxony, the percentages of clay substance decreases with depth, and that the clay grades into fresh rock below.

Summary of Facts in Support of Theory of Kaolinization by Weathering Processes.—The facts in support of kaolinization by simple weathering processes are:

1. The possible alteration of feldspar to kaolinite by water, whether containing carbon dioxide or not.

2. The observed transition with depth of kaolin into unaltered parent rock in many cases. This is seen in the feldspar deposits of North Carolina, Maryland, Pennsylvania, Delaware and Massachusetts.

3. The fact that in the United States practically all of the commercially valuable kaolin deposits lie south of the glaciated areas, in other words, in a region in which residual clays still remain, is significant.

Objections to Theory of Kaolinization by Weathering.—While these facts and examples show that kaolin may be formed by weathering, there is no intention, at least on the writer's part, to claim that all kaolin is formed in this manner. And, while the theory of weathering has received wide and continued acceptance, opponents have not been lacking.

Among the most active opponents has been H. Rösler, who has sought most earnestly to discredit the weathering theory. His objections are given below, each one being followed by the corresponding counter argument.

1. Kaolin passes into fresh rock horizontally, but never does so with depth.

This statement is absolutely disproved by many Amer-

[1] Zeitschr. f. prak. Geol., XV, 1907.
[2] Beskrivelse of Kaolinslemmerit Rabekkegard paa Bornholm.
[3] Zeitschr. f. prak. Geol., 1909, p. 457.

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ican and foreign occurrences which Rösler ignores. It may be noted also that some of the kaolin deposits which he cites to prove this theory are said by others to grade into solid granite below.[1]

2. In the weathering of feldspars, only lime and soda are dissolved and removed, while the potash content is retained. This, he claims, is shown by the complete absence of potash in surface waters and springs (hot springs and acid ones excepted), and also by the fact that analyses of the weathered product show the same amount of potash as the fresh rock. Moreover, Rösler argues that potash is only extracted from the weathering products of feldspar when they come in contact with organisms.

This statement is also incorrect, for G. P. Merrill[2] has shown, by a comparison of the analyses of igneous rocks and their derived clays, that the residual clay contains from 29 to 91 per cent. less potash than the fresh rock. The mere presence of potash in the clay does not necessarily represent undecomposed mineral grains for it may be soluble potassium carbonate held there by adsorption.[3]

3. Water, even if carbonated, can hardly effect extensive decomposition because the attacked mineral surfaces soon become covered with a protective scum of weathering products.

This argument hardly needs recognition. It might occur in laboratory work as shown by Cushman,[4] but in the rock where frost action, percolating waters and other forces are exerting a disturbing action, this skin will be broken up.

4. Rösler, quoting Haushofer's experiments,[5] claims that the rate of decomposition calculated by the former is too slight to bring about much decomposition of the feldspar, and that even CO_2 would hardly accelerate the action.

He (Rösler) neglects the time element which might

[1] See Gräbert, Zeitschr. prak. Geol., 1909, p. 142; Winkel, Beskrivelse of Kaolinslemmerit Rabekkegaard paa Bornholm. Zeitschr. prak. Geol., XV, p. 10, 1907.

[2] Rocks, Rockweathering and Soils.

[3] Binns, Trans. Amer. Cer. Soc., VIII, p. 198.

[4] Trans. Amer. Cer. Soc., Vol. VIII.

[5] From Jour. prakt. Chemie, 1868, CIII, p. 121.

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have been great, and that it has been definitely shown that carbonated waters, as mentioned above, do attack feldspar.

5. It is said that little is definitely known regarding the constitution of the products of feldspar decomposition formed by weathering; and that it is possibly an alkaline aluminum silicate rather than kaolinite, for the alkali content, especially the potash in the products of feldspar decomposition, often exceeds the water content, and is never absent.

This statement hardly needs refutation, at least it would seem so to those who are familiar with American kaolins, for in none of these does the alkali content exceed the water percentage, and, moreover, the presence of alkalies, even to the extent of several per cent., proves nothing against the weathering theory. As already mentioned the potash might be held in the clay by adsorption, or it might be locked up in muscovite or sericite, which remains undecomposed long after the feldspar has kaolinized.

6. Apatite is said to be unattacked by weathering processes, but decomposed and removed by pneumatolytic action.

This is not altogether true, for G. P. Merrill has shown by analyses of a series of fresh and weathered rocks that in most cases there is a loss of phosphoric acid which, in the figures given by him, ranges from about 11 to 68%. On the other hand, as some of Merrill's analyses show, there is occasionally either no loss or a positive gain in phosphoric acid, a fact also pointed out by Brauhauser,[1] in the case of the Kegelbach granite, which showed more P_2O_5 in the weathered than in the fresh rock.

Endell,[2] however, corroborates Merrill as regards the loss of P_2O_5 in most cases, but his examples often lack weight, because the analyses of fresh and kaolinized rock do not, in every case, appear to be taken from the same locality.

[1] Jahreshefte des Vereins für vaterlandische Naturkunde in Württemberg, 64. Jhg. 1908, 5, 17.

[2] Sprechsaal, XLII, No. 34, p. 495, 1909.

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7. It is said that kaolinization, which Rösler regards as distinct from weathering, is never preceded by mechanical disintegration, while in rock weathering this always occurs.

This statement is hard to prove as in most cases the rock is so decomposed that one cannot tell whether or not disintegration had occurred.

8. In the kaolinization of a porphyritic rock, the phenocrysts are altered before the ground mass is affected, while in weathering this order would be reversed.

As many kaolinized rocks are not porphyritic, the statement, if true, would have no general application. The so-called feldspar beds of the New Jersey Cretaceous already referred to show that both the coarse and fine feldspar fragments have undergone decomposition at the same time.

9. The biotite in kaolin is fresh and rarely bleached, and hence, kaolinization cannot be due to weathering.

None of the American residual kaolins show fresh biotite; and, furthermore, if garnet is present, it is more or less decayed.

10. Rösler claims that in foreign kaolins he finds secondary siderite, tourmaline, pyrite, topaz, and fluorite, which must be secondary because they are not found in the surrounding rock, and hence the kaolin cannot be a product of weathering.

This claim can be met with the argument that topaz, fluorite and tourmaline are vein minerals produced by gas-aqueous action. Their distribution is, therefore, often confined to vein fissures, and it is in such parts of the rock that the weathering agents penetrate more readily. This would account for the association of kaolin with pneumatolytic minerals.

The pyrite might be deposited in the clay by an adsorptive process as shown by Sullivan,[1] and its later origin explains nothing as regards the formation of the kaolin.

11. Minerals, like iron oxide and monazite, are, it is

[1] Econ. Geol., I, p. 67, 1906.

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claimed, easily weathered, and hence their presence in kaolin shows that it could not have been formed by weathering processes.

The statement that monazite is an easily weathered mineral can hardly be regarded as correct as it is found in residual soils in North Carolina as well as in the alluvial sands which are composed of the more resistant minerals from these soils. In fact, monazite grains occur in sufficient quantity in these sands to make their extraction profitable.

Iron ore may be present in any residual clay as a product of concentration of meteoric waters.

12. Finally, it has been argued that in some regions where kaolin has been formed from granite, the rock in the surrounding area is broken down to a sandy mass, but not to a kaolin, which sandy mass represents a weathering product.

This is no argument against the theory of weathering. It might simply indicate that in any particular rock all parts of the mass had not been altered to the same degree, and as disintegration often precedes decomposition, the sandy product may simply represent an earlier stage in the decay.

After considering all these arguments, both *pro* and *con*, I still believe that kaolin can be formed by ordinary weathering processes, and that many of the economically valuable kaolin deposits have originated in this manner.

KAOLINIZATION BY POST-VOLCANIC EMANATIONS.

This theory assumes that the kaolin has been formed from feldspar by the action of heated waters (possibly of acid character), or by gases, both of igneous origin, acting either singly or together. These kaolinizing agents are supposed to have been given off by some igneous mass, and, according to the different theories, the depth below the surface at which the kaolinization occurs is not the same in all cases.

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This theory in different forms has been advanced by a number of writers and investigators, and is often spoken of as the pneumatolytic theory. The term just mentioned is, however, only applicable to kaolinization occurring at great pressure and high temperature.

Advocates of and Examples Illustrating Kaolinization by Volcanic Emanations.—1. Probably the first to assign a pneumatolytic origin to kaolin was von Buch,[1] who sought to apply this explanation to certain German kaolin deposits because they contained fluorite.

2. Forchhammer[2] offered a similar theory for the occurrence of Scandinavian kaolins, but thought that they were formed by the action of hot water vapors alone.

3. Daubree, the French geologist, was another advocate of the pneumatolytic theory of the origin of kaolin.[3]

4. Some years later, the theory was exploited anew by J. H. Collins,[4] who sought to apply it to the kaolins of the Cornwall district of England. Mr. Collins, to verify his theory experimentally, exposed feldspar to the action of hydrofluoric acid, as a result of which it was converted into a hydrated silicate of alumina mixed with soluble fluoride of potassium, while pure silica was deposited on the sides of the tube. He also found that orthoclase was more readily attacked than either albite or oligoclase.

The following analyses show the effect of 96 hours of treatment of orthoclase with hydrofluoric acid at 60° F. No. I is the original felsdpar, No. II is the inner layer of altered feldspar, and No. III is the outer layer of altered feldspar.

[1] Beschreibung des Harzes, 1824.

[2] Zusammensetzung der Porcellanerde und ihre Entstehung aus Feldspath, Pogg. Ann., XXXV, p. 331.

[3] Compt. rend., LXVIII, p. 1135 and Etudes synthetiques de geologie experimentale, 1879; also Les eaux souterraines aux epoques anciennes, Paris, 1887.

[4] Mineralog. Mag., VII, p. 123, 1887.

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	I	II	III
SiO_2	63.70	49.20	44.10
Al_2O_3	19.76	35.12	40.25
K_2O	13.61	0.12	0.25
Na_2O	2.26	trace	trace
Fe_2O_3	0.71	trace	trace
H_2O	trace	14.20	15.01
	100.04	98.64	99.61

The analysis of the outer layer, it will be noticed, approximates kaolinite in its composition. Under the microscope it showed no hexagonal scales but contained a number of colorless minute cubes which were supposed to be fluorspar.

It is interesting, in this connection, to note that G. Hickling[1] repeated Collin's experiments and claimed to have been unable to obtain a product that was like kaolin either in appearance or composition.

5. Other adherents of the pneumatolytic theory have not been wanting, for it was accepted by Mallard to explain kaolinization in certain tin deposits,[2] and also by Auscher and Quillard in their work "Technologie de Ceramique," Paris, 1901.

That kaolinite can be formed from feldspar, through the action of hot magmatic waters, has been observed in the study of many ore deposits.

6. Lindgren[3] states that kaolinite may be formed by the metasomatism or replacement of orthoclase, albite or soda-lime feldspars with the liberation of silica, the reaction in the first case being expressed as follows:

$$6(KAlSi_3O_8) + 6H_2O + 3CO_2 = 3(H_4Al_2Si_2O_9) + 3K_2CO_3 — 12SiO_2.$$

According to the same author, ferromagnesian silicates,

[1] Trans. Inst. Min. Engrs., England, XXXVI, p. 10, 1908–09.

[2] Etudes sur les gisements stanniferes du Limousin et de la Marche.

[3] Metasomatic Processes in Fissure Veins, Amer. Inst. Min. Engrs., Trans., Feb., 1900.

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and even quartz, as shown by the altered rock adjoining a recent vein near Boulder, Mont., may be converted into kaolinite. The mineral is very finely divided. The same author remarks on the frequent occurrence of kaolinite in cassiterite veins, although here it may be simply a secondary alteration of topaz.

7. It is known to occur, together with sericite, in veins of the pyritic galena-formation of Freiberg, Saxony; in some veins of *propylitic* character, as at Cripple Creek, Colo., and in veins where the action of stronger reagents, such as sulfuric acid, seems probable (Summit District, Colo., De Lamar, Idaho). None of these represent deposits of commercial value.

But while kaolin may be formed by metasomatism through the agency of ascending wâters derived from igneous rocks, the work of Lindgren[1] has shown that it cannot be formed under deep-seated conditions, and cannot, therefore, be of pneumatolytic origin, like tourmaline, topaz or cassiterite.

8. Ransome[2] has described an interesting occurrence of kaolin in the National Bell Mine, where it forms a snowy white powder, of minute crystalline scales. "As seen in the upper workings in 1899 it occurs as filling fissures in the country rock or as a filling between the fragments of brecciated zones near the ore bodies. It was apparently in these cases deposited later than the ores, partly taking the place of the clay gouge commonly associated with post-mineral movements in other localities.

"As an original constituent accompanying the ores, kaolin occurs abundantly in the stock deposits of the Red Mountain district. . . . It appears to have accompanied the ores to the greatest depths there attained (about 1300 feet). It was evidently derived from the country rock adjacent to the ore bodies as a product of its alteration by thermal waters."

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[1] Econ. Geol., II, p. 105.

[2] U. S. Geol. Surv., Bull. 182, p. 73, 1901.

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Ransome further states on p. 234: "The National Belle Mine has long been noted for the abundance and purity of the kaolin found in its workings."

This is the material that was described optically by Reusch.[1]

The composition of it as given by Hillebrand (I) and Hiortdahl (II) and quoted by Ransome is given below:

	I	II
SiO_2	46.35	45.57
Al_2O_3	39.59	41.52
Fe_2O_3	0.11	.....
H_2O	13.93	13.58
F	0.15	.....
	100.13	100.67

The foregoing facts seem to warrant the assumption that kaolinization has been effected by ascending waters of probable, if not undoubted, magmatic origin. But whether the commercially valuable deposits of kaolin have thus originated is another question.

9. Rösler[2] has put forth the theory that not only have the kaolins been formed in this way, but that the agents were of gaseous or gas-aqueous character.

If this is true, they must also have been formed at great depths, and are now exposed at the surface because of the erosion of the overlying rocks.

Rösler's theory has not remained undisputed, and the publication of it has started a war of discussion in the foreign scientific press between the advocates of the several theories in which the participants have been demanding nothing less than absolute surrender from their respective opponents.

Rösler's premises are, firstly, that kaolinization is a

[1] Neues Jahrb. für Min., II, p. 70, 1887.
[2] Neues Jahrb. für Min. Geol. u. Pal., XV, Beilage Band, 2nd Heft, pp. 231–393.

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pneumatolytic or pneumato-hydatogenetic process, totally distinct from weathering, and secondly, that the latter in no case causes feldspar to change to kaolin. Some of his arguments have already been recited (see pages 57-61 incl.) and others are:

(*a*) Kaolin deposits extend to too great depths to be due to weathering.

(*b*) Weathering does not remove potash from feldspar, and since kaolins contain little or no potash, they must have been formed by other agents, to wit, pneumatolytic or pneumato-hydatogenetic ones.

(*c*) Weathering changes granite to a clayey sand and not to a clay.

(*d*) Biotite found in kaolin is often fresh, while weathering would surely decompose it.

(*e*) Kaolin contains sericite as a secondary formation, and, as this is never produced by weathering, it must be a gas-aqueous product.

(*f*) Kaolin deposits are associated with fissures, or exhibit a form indicating such association. This shows their close relation to the pathway up which the kaolinizing waters or vapors traveled from below.

Conclusions Concerning Kaolinization by Pneumatolysis.—Mr Rösler's work indicates that he has gone to considerable trouble to prove his theory, and yet his attempted sweeping application of it, his uncompromising attitude towards other theories, and his total neglect of all American occurrences make one feel that his enthusiasm has led him to assume rather narrow views.

It is perfectly possible that kaolinite may be formed from feldspar through the action of magmatic waters, and it is possible that *some* of the commercially valuable deposits of kaolin found in the world may have originated in this manner, but I feel less sure of it now than I did a few years ago.

Where one finds kaolin masses closely associated with fissure veins as in Cornwall, England, and extending to a depth of several hundred feet, one naturally is willing to

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believe that these may be examples of the theory so ardently expounded and actively defended by Rösler. And yet the recent work of Hickling[1] may, perhaps, with reason cause us to regard the Cornwall kaolins as weathering products after all for, according to him, the kaolin is a surface sheet, covering the irregularly corroded surface of the solid granite, and moreover, there is no constant relation between fissures and kaolin, some fissures in the solid, fresh granite being free from kaolin. The whiter color of the deeper clay, Hickling believes, is due to the fact that the surface waters have not carried down enough oxygen to decompose the biotite and oxidize the iron in it.

In the case of the Carlsbad kaolin deposits, which, because of their association with the springs, one might suppose to be due to the action of waters ascending from below, Stremme has pointed out that only seven of the deposits show a parallelism with the hot springs fissure, while twelve of them lie at some distance from this line.

But a most serious objection to the contemporaneous origin of kaolinite, tourmaline, topaz, and cassiterite by pneumatolytic processes, is the evidence given by Lindgren,[2] regarding the relative depths at which the above-mentioned minerals are formed. This would seem to conclusively dispose of the theory without any additional disputative evidence.

FORMATION OF KAOLIN BY WATERS CONTAINING CARBON DIOXIDE.

This view, which may be regarded as a modification of the theory just described, was advanced by C. Gägel and H. Stremme[3] to explain the kaolinization of granite by the cold acid waters of the Elizabeth Spring near Carlsbad in Bohemia. At this locality a funnel-shaped opening of about 30 to 40 meters in diameter had been excavated, at the base of which a shaft was being sunk. The walls of the pit consisted entirely of snow-white kaolin which retained the structure of the original granite to a large extent.

[1] Trans. Inst. Min. Engrs. (England).

[2] Loc. cit.

[3] Centralblatt für Mineralogie, Nos. 14 and 15, pp. 427–475 and 467–475, 1909.

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Analyses showed that the potash content of the kaolin was only about 1/15 that of the granite, soda about 1/30, magnesia and lime about 1/2, and phosphoric acid about 1/2. The iron content was in part less, in part greater than that of the original rock.

The author believed that it represents a simple case of kaolinization by water containing CO_2. There is no evidence of pneumatolytic action, nor of the work being done by surface water as indicated by the absence of superficial iron discoloration.

Action of Hydrochloric Acid on Feldspar.—As having some bearing on the kaolinization of feldspar by acid waters, we may refer to the experiments of Tucker,[1] who found that powdered feldspar, when treated with very dilute hydrochloric acid (0.075%), for ten days at ordinary temperatures, is decomposed into a milky white substance indistinguishable in appearance from the china clay of commerce, and containing scales which were micaceous in character. Shap granite, Falmouth granite and china stone were similarly decomposed, yielding a material quite like kaolin.

Such a decomposition will take place at ordinary temperatures with nitric, sulphuric, hydrochloric and hydrofluoric acids, and, in the case of feldspar and granites, with water containing carbonic acid.

KAOLINIZATION BY SWAMP WATERS.

This theory postulates a close association between kaolins, and deposits containing lignite or carbonaceous matter. It is claimed that the waters leaching out of such deposits contain humic and carbonic acid, and organic matter, but a deficiency in oxygen. Now if such a solution seeps down into some underlying feldspathic rock, it attacks the latter, causing its alteration to kaolin.

Organic Coloring of Kaolins Taken as Proof.—The advocates of this theory claim that the waters, because of their composition, leach out the iron from the rock, and at the same time contribute some organic matter to the clay,

[1] Quoted by Hickling. Trans. Inst. Min. Engrs. (England).

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tinging it red or gray. As evidence of this Stremme[1] points to the fact that some kaolins, as those of Carlsbad and Halle, have red and gray colors which he says they would not show, if they had been produced by post-volcanic processes. Stremme claims that the coloring matter in these kaolins must be organic for the colors disappear when the clays are exposed to the air or are ignited. The source of this coloring matter is supposed to have been the bogs which formerly covered the surface in this district. He, therefore, advances this view to explain the origin of many kaolins, including those at Adolfshütte bei Bautzen, Carlsbad, Löthain, Schletta bei Meissen, Halle a. d. Salle, and Muldenstein.

Stremme ascribed this kaolinizing action to the organic matter in the waters from Tertiary swamps.[2] He claims that at some localities these carbonaceous matters, which overlaid these kaolin deposits, have been removed by erosion, and only the alleged product of their work remains.

The only application of this theory in the United States is the case of certain kaolinized pegmatite veins on Manhattan Island, New York, which are believed by Julien to have been formed in this manner.

Difference in Effect of Swamp and Surface Waters.—The effect of swamp waters differs from the ordinary weathering work of surface waters in the following ways:

1. The total iron and magnesium of the kaolin is increased in weathering, but decreased by the leaching of swamp waters.

2. Weathering changes the iron to limonite, but swamp waters alter it to pyrite and siderite.

3. It is believed that the high alumina percentages of the kaolin formed by swamp waters shows that in its formation there were fewer mechanically active forces than in the case of weathering, as otherwise much of the clay sub-

[1] Zeitschr. prak. Geol., XVI, p. 126, 1906.

[2] Tonind. Zeit., XXXIII, p. 1607, 1909; Zeitschr. prakt. Geol., Mar., 1908; Ramann, Bodenkunde, 2d Ed., Berlin, 1905, holds a similar view. See also Berg. Monatsber. d. Deutsch. Geol. Ges., 1906, p. 56; Hochstetter, Karslbad, seine geognost. Verh. u. S. Quellen; 1856; and Weiss, Zeitschr. f. prakt. Geol., XVIII, p. 353, 1910.

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stance formed would have been washed out, leaving an excess of silica behind.

4. The cause of the low iron content of these kaolins is thought to be due to the strong leaching effect of these swamp waters.

Objections to this Theory.—While there is a strong possibility that some kaolins may have been formed in the manner outlined, it is difficult to positively ascribe such an origin to any unless there is proof of the existence, present or past, of an overlying carbonaceous deposit or swamp. Kaolin can be formed by simple weathering, and in this process, carbonic acid waters may play a rôle. None of the American kaolins show any evidence of a genetic relation to swamps or coal beds, and the pre-Cambrian kaolins of Wisconsin,[1] derived from the weathering of schists, and overlain by Cambrian sandstone, were not associated with deposits of decaying vegetable matter as land plants were not then in existence.

The theory has been most energetically disputed by Rösler, who claims that Stremme's analyses do not prove kaolinization, but in view of the fact that crude kaolins may show considerable variation in their composition, this objection cannot be a very serious one. Furthermore, he claims that Stremme's analyses show by their high alkali content that we are here dealing with minerals like sericite and not kaolin. This likewise seems to me to have little weight as the white residual kaolins, especially those found in the United States, may show 2 to 3% of alkalies. To say that these white residual plastic clays were not kaolins would be absurd.

The brown or gray discolorations might, as Rösler argues, be due to surface waters, and not extend to unlimited depths.

It should be said in Mr. Stremme's favor, that while he firmly believes in kaolinization by swamp waters, and considers that many European deposits have been formed in this manner, still his views are temperately expressed,

[1] Buckley, E. R., Wis. Geol., and Nat. Hist. Surv., Bull. 7, Pt. 1, 1901; and Ries, Ibid., Bull. 15, 1906.

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and he shows no desire to insist that *all* kaolins have been thus formed.

KAOLINIZATION BY SULPHATE SOLUTIONS.

Kaolinite is found abundantly in the Goldfield, Nevada, ore district, and while it is formed by weathering processes in the zone of oxidation, it is not confined to this belt, but is also present in the sulphide zone, and as a constituent of the unoxidized country rock in the vicinity of the ore bodies.

Example of this Process of Weathering.—Ransome[1] states that "The dacite from the 230-feet level of the Combination mine, contains 24% of kaolinite by weight. In such altered rocks the kaolinite forms very minutely crystalline aggregates of feeble birefringence as seen in thin sections under the microscope. These aggregates have rather ill-defined boundaries and the kaolinite is intimately and contemporaneously crystallized with quartz, alunite, and pyrite. A very large part of the altered dacite in the vicinity of the ore bodies near Goldfield consists of these four minerals in varying proportions. A similar alteration has affected the latite . . . in the bottom level (280 feet) of the January mine."

Ransome furthermore says: "That the intimate association of the alunite with kaolinite at Goldfield has a bearing on the problem . . . "

Lindgren (Econ. Geol., II, 120, 1907) has recently intimated that although he himself formerly referred to the mineral as characteristic of certain classes of veins, kaolinite should not be considered as a gangue mineral of any class of ore deposits except those formed under the influence of oxidation. In a subsequent paragraph, he somewhat modified his statement by the expression of belief that "kaolin is rarely formed by alkaline hot water at any considerable depth below the surface."

"The preponderant weight of careful observations

[1] U. S. Geol. Surv., Prof. Paper 66, p. 127, 1909.

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made during the last few years is unquestionably on the side of the thesis thus moderately stated; and the occurrence of kaolinite at Goldfield where the intimate association of the mineral with the alunite, gold, sulphides, tellurides, and sulphantimonites, as determined by microscopical work, shows that all were formed at the same time and by one general process, is an additional point against what has been called the direct volcanic hypothesis."

KAOLINIZATION BY WEATHERING OF MUSCOVITE.

In most of the theories, which have been advanced concerning the origin of kaolin, it has been considered to be, in most cases, a decomposition product of feldspar, hence, a theory which proposes muscovite as its source is unique. Such a one has been advanced by G. Hickling,[1] for the Cornwall kaolins.

Evidence in Support of this Theory.—His reasons for believing that the kaolinite is derived from mica and not from feldspar are as follows:

1. Microscopic examination of the feldspars of decomposed granites show nothing that he can identify as kaolinite.

2. The kaolinite crystals are only seen in the fine powder which gives rise to the clay, and, therefore, its development takes place in the clay.

3. The micaceous habit of the kaolinite crystals.

4. There is no visible difference in form between the kaolinite and muscovite.

5. The curious vermiculite forms are evidence that the kaolinite was not deposited from solutions.

6. The kaolinite prisms show every variation in birefringence, from that of muscovite to *nil*.

7. Prisms are found which are muscovite at one end and kaolinite at the other.

8. The experiment of A. Johnstone[2] showing that muscovite, exposed to water containing CO_2, changed to

[1] Trans. Inst. Min. Engrs. (England), XXXVI, p. 10, 1908–9.

[2] Quart. Jour. Geol. Soc., XLV, p. 363–368, 1889.

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hydro-muscovite, and the hydrated condition of the muscovite in the clay is in keeping with this theory.

Relation between this Theory and that of Kaolinization by Weathering.—Since, in this theory, muscovite represents the first stage in the weathering of feldspars, and the kaolinite the second, this theory may be regarded as a modification of the original theory of kaolinization by weathering.

V. Selle[1] has expressed a somewhat similar opinion at an earlier date, claiming that weathering and kaolinization were analogous processes, differing only in degree, but that in both cases mica is found as an intermediate product of the final decomposition of feldspar, and this mica is again resolved into kaolinite.

The Weakness of the Theory.—Interesting as Mr. Hickling's explanation of kaolinization is, one cannot fail to see some difficulties in its acceptance. In the first place his proof is based in part on the optical properties of two minerals which differ but slightly optically, and can only be studied satisfactorily with very high powers. Indeed, some investigators claim that the theory of the pneumatolytic origin of kaolin has received more recognition than it deserves, because in not a few cases sericite has been mistaken for kaolinite.

Secondly, sericite is not usually regarded as a weathering product of feldspar.

SUMMARY.

It will be seen from what has been said that there are now a number of theories to explain the origin of kaolin.

On the one hand we have the oldest or weathering theory; on the other we have five or six theories which hold that kaolinization is a different process from weathering, but differ strongly regarding the agents or processes involved in kaolinization.

With one exception all theories concerning the origin

[1] Sprechsaal, XL, p. 463, 1907.

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of kaolin agree in regarding feldspar as the parent mineral, but each theory differs in regard to the mineralogical and chemical changes involved. Thus in weathering, an extensive leaching of certain constituents, especially lime, magnesia and alkalies may occur, while the iron is fixed as oxide or hydroxide, very little of it being removed. In the case of post-volcanic emanations, where weak acids and much water are present, but a deficiency of oxygen, iron may remain as pyrite. In the decomposition of rocks by swamp waters, containing carbon dioxide but deficient in oxygen, the iron may be leached out.

A careful sifting of the evidence would seem to indicate that the kaolin might be formed according to any one of the three important processes, *viz.*, weathering, volcanic waters, and vapors, or acidulated waters from coal beds and swamps.

The mere fact that the bottom of a deposit has not been reached is no proof against the theory of weathering, for it is well known that this action sometimes extends to great depths, far greater than that thus far reached in the mining of any known kaolin deposits.

The absence of coal beds over the kaolin deposit is not necessarily evidence that they never existed there.

The writer's personal opinion is that all of the workable kaolin deposits of the United States, and probably many of those of Central Europe, are the work of surface waters, whether they entered direct from the surface or filtered first through a swamp or bed of peat.

That kaolin may be formed by post-volcanic vapors or waters is no doubt true, as shown by the formation of this mineral below ground-water level in the wall rock of many veins, and the turquoise deposits of New Mexico, but whether any commercially valuable deposits have thus originated remains to be proven.

Whatever theory may be finally adopted it is of the highest importance that the theory should be made to fit the facts, and not the facts made to fit the theory.

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FLUXES AND FUSION.[1]

By Ross C. PURDY, Columbus, Ohio.

INTRODUCTION.

Scope.—I wish to consider this subject as it applies to ceramics alone. These same considerations would apply (with some few additions) to all industrial studies which involve silicate fusion. Since the conditions attending the completeness of, as well as the reactions coincident with the fusion of the glass, silicate enamels, slags, cements, etc., etc., are so different and offer so many phenomena, it would be unwise to attempt a comprehensive discussion of the general topic—silicate fusion. In fact, I beg to confine our thought entirely to the most simple of the silicate fusions with which the ceramist has to deal, such as those which take place in the simple mixtures of kaolin, feldspar and flint of which china, porcelain, and all other white ware bodies are composed.

GENERAL PRINCIPLES INVOLVED.

At the outset let me call attention to a few general principles that will be involved in this informal discussion and which are generally known.

Molecular Kinetic Energy.—I must confess unwillingness to either deny or acknowledge full belief that each molecule of a solid rock crystal is in perpetual motion and anxious to bombard the sides of a containing vessel. Physicists claim and offer unimpeachable proof that such molecular activity is true in the case of gases, and they claim that if it were not for molecular cohesion, this same phenomena would be more apparent in liquids and solids. Such phenomena as gas pressure, surface tension, etc., are offered as evidence of molecular kinetic energy in each of the three states of matter, *viz.*, gaseous, liquid and solid.

[1] Presidential address delivered at the 12th Annual Meeting but which, owing to misunderstanding, was not published.

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When a solid is heated it generally expands and as the temperature of that solid is increased, the kinetic energy of the molecules is increased, until finally this kinetic energy is sufficient to overcome the molecular cohesion, the result being a change of state, as, for instance, from solid to liquid.

External pressure offers a counter-force delaying this change in state. Barus, I believe, found that in case of basalt a pressure of 40 atmospheres counteracted the influence of 1° centigrade rise in temperature. In defining such terms as melting point, it is necessary, therefore, to take cognizance of both temperature and pressure.

Melting Point.—As a definition of melting point, I offer the following: With *constant pressure,* the temperature required to increase the kinetic energy of the molecules of a solid sufficiently to overcome their mutual cohesion is the melting point of that solid at that pressure.

A definite melting point of a substance requires, therefore, a distinct change in phase at a definite temperature-pressure point. Most solid crystals exhibit this phenomena. That a study of fusions may not be too easy, all solid substances do not have a definite melting point, that is, they do not change phase when passing from what we customarily call a solid state to that known as fluid. We might picture a rigid fluid, rigid in this case referring to high degree of viscosity of the fluid in which there is no definite arrangement of the molecules. Such solids are said to be amorphous.

Glass is a highly viscous fluid, *i. e.*, a rigid fluid, and not a solid in the same sense as is implied when speaking of crystals.

Fusion.—When a viscous fluid is heated there is no change in phase. It is merely a change in degree of viscosity. Since, as in case of glass, we have no change in phase, the change being merely one of relative degree of viscosity, it is easy to see why this change is gradual, involving nothing that would mark a definite point. Such a change is a function of temperature and pressure, being

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at all times directly proportional to the temperature and inversely to the pressure. A change from a rigid fluid to a less viscous fluid is a gradual melting; this is fusion.

FLUXES.

Popular Conception.—According to the usual conception, a flux is a solid substance which, when blended with a more refractory solid, will cause a lowering of the melting point, or in other words, will increase the ease of fusion of the second substance. Sodium carbonate blended with clay makes possible the liquefaction of the clay. We say in the laboratory, the carbonate fluxes the clay. In silicate fusion, the carbonate is present in such excess that a portion of it undoubtedly is the first to melt and when melted serves first as a solvent and then as a reacting agent, causing chemical disintegration of the clay. Suppose that in place of the 10 to 1 mixture we take a mixture of 1 of sodium and 10 of clay. Will the sodium fuse the clay? Yes, but not completely. Has the sodium fluxed the clay and is the sodium in this case a flux? So far as we know it has not.

Take another example if you will, as, for instance, a mixture of wollastonite ($CaSiO_3$) and silicon oxide. Wollastonite inverts at 1200° C. into a pseudo-hexagonal form and this second phase melts at 1520° C. Pure SiO_2 (tridymite) melts at about 1600° C. Any mixture of these two substances will fuse at a temperature lower than the melting point of either, and the most fusible mixture of the two is 76.6 $CaSiO_3$, 23.4% SiO_2 melting at 1420° C.

If these two minerals are thoroughly blended, fused to a molten fluid and then cooled to a rigid condition again, we would still have pure SiO_2 and pure wollastonite chemically unaffected; merely more intimately mixed. In other words, these two minerals do not react chemically one with the other when fused together. Repeated fusions in this case would merely cause a more intimate mixture and yet the ease with which these fusions can be obtained is increased with each successive re-fusion. Since we

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have greater ease of fusion and yet no chemical reaction between these two substances, this greater ease must result from the only other factor involved, *i. e.*, more intimate mixture of the two. This case must, therefore, be an exception to the usually conceived notion of fusion. Fusion does not always involve chemical reaction.

The Flux.—To go a little deeper in the case of the wollastonite-silica mixtures, their liquidus, after Day and Shepherd, is here represented.

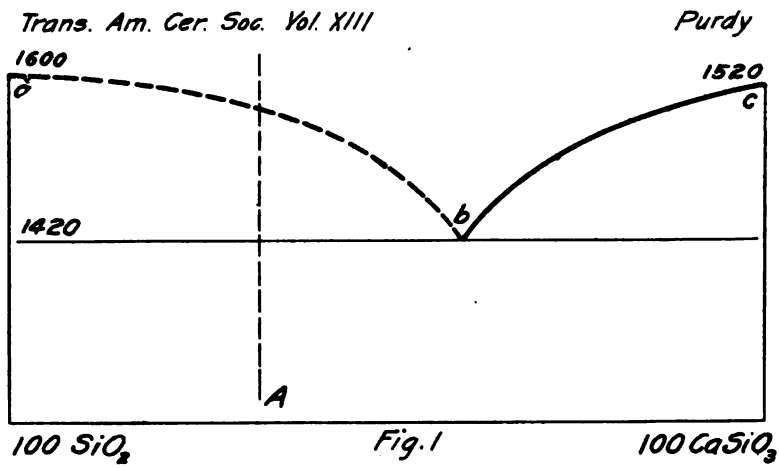

Fig. 1

The dotting of liquidus AB is to indicate that, owing to the extreme viscosity of the melts, making diffusion slow, the exact melting point of these mixtures is uncertain. The horizontal line drawn through the eutectic indicates that as these several mixtures were heated, a melt consisting of the two components in eutectic ratio was noted at approximately the same temperature, 1420° C.

Suppose we start with a thoroughly blended mixture of SiO_2 and wollastonite, such as A, and heat it up to 1420° C. Until this temperature has been attained, the powder has been merely sintering but at 1420 fusion begins, *i. e.*, a solution is formed. This solution is going to act as a

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solvent in which the component present in excess of that required for the eutectic will be dissolved.

This solvent is neither SiO_2 nor $CaSiO_3$ taken alone; it is the eutectic mixture of the two. Just as the excess sodium compounds are the solvent in ordinary silicate fusion so is this eutectic mixture of SiO_2 and $CaSiO_3$ the solvent in this case. The only essential difference in action of these two solvents toward their respective solutions is in miscibility, viscosity and liquefaction—factors which effect a difference in rapidity of the fluxing action but not a difference in kind. In this case the eutectic mixture of the two components is the solvent and, hence, the flux.

No Chemical Reaction and No Eutectic.—In the two instances cited, we have two cases of fusion involving two essentially different phenomena—in the first, chemical reactions resulting in new compounds; in the second, no chemical reactions, the flux being the eutectic of the two components. There is a third important case in which neither chemical reactions nor eutectic mixtures enter as affecting factors, namely, isomorphous mixtures.

Day and Allen have shown that anorthite and albite feldspar form isomorphous mixtures, the liquids of which is as shown (p. 80). In this case the more fusible of the components is the flux.

Pottery Mixtures.—Mixtures of kaolin and feldspar have been shown by Simonies to be isomorphous giving a curve similar to Day and Allen's feldspar curve. Mixtures of feldspar and flint have a slight eutectic and those of kaolin and flint a decided eutectic. In none of these cases have we evidence of chemical reactions due to interreaction between the components present.

What takes place then, when a porcelain mixture vitrifies? In porcelain consisting only of the three components—flint, feldspar and kaolin—fusion is simply the result of the formation of eutectic mixtures, and liquefaction of the excess feldspar both acting as the solvent for excess clay and flint.

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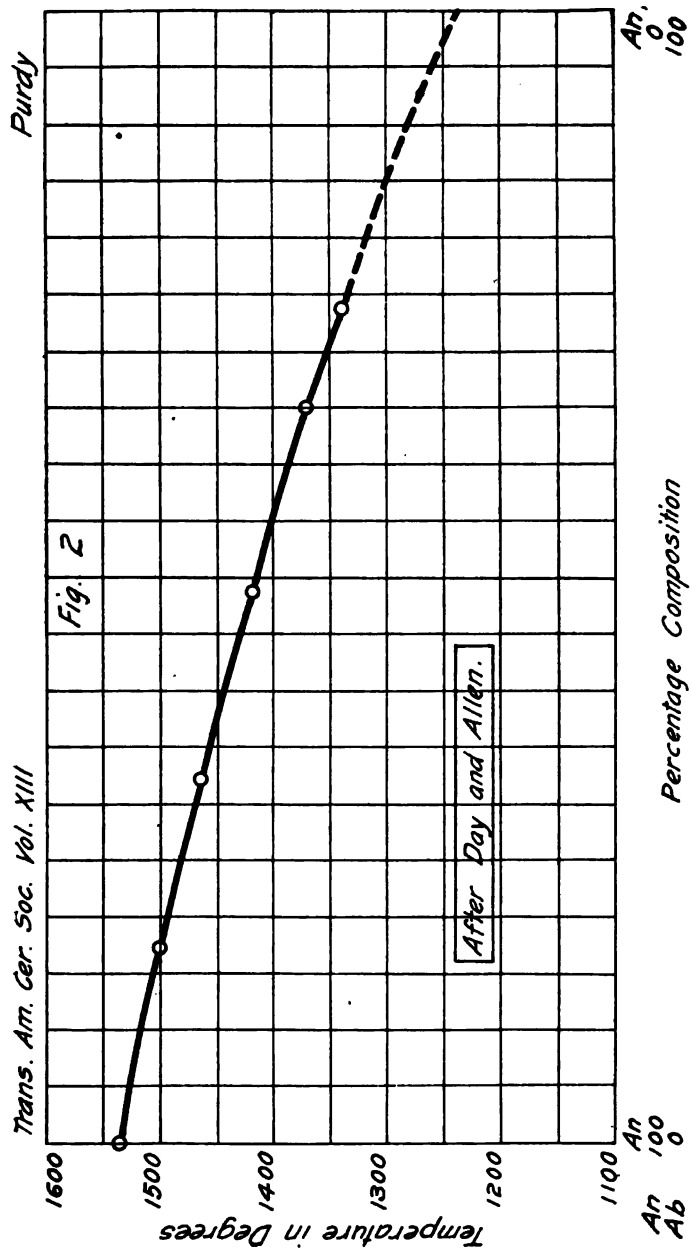

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There are a few physical-chemical changes in phases which occur in the fusion of porcelain mixtures that are of importance but which need not be involved in discussion of the nature of the fusion. The two most important of these changes are the inversion of quartz to tridymite, and decomposition of the kaolin into sillimanite and free silica.

CAPITULATION.

(1) We have defined a flux as that substance or mixture of substances which, in a given mixture, is the first to liquefy and become the solvent for the excess components.

(2) We have defined fusion as the making fluid of a substance or mixture of substances, whether they be crystalline or amorphous. Fusion is a broader term than melting, in that melting has a definite temperature point while fusion may or may not have such a point. In crystalline silicates, it is very difficult, but not always impossible, to determine the melting point, their melting being so sluggish as to appear to be mere fusion without definite melting points. High viscosity of the melts and consequent difficult miscibility is responsible for this.

PRACTICAL EXAMPLES.

As practical examples, illustrating this new idea or definition of a flux, I will cite only two, and these, to avoid appearing biased, will not be of my own findings.

Work by Simonies.—In Sprechsaal No. 30, '07, Simonies published the following curves plotted on a triaxial diagram (see Fig. 3). The lines running in parallel diagonally across the diagram are those of equi-refractoriness. The line AB is what may be termed a eutectic axis; it is drawn from the clay-quartz eutectic to the feldspar apex. The numbers are the cone deformation points of the mixtures.

Attention is especially directed to the fact that the equi-refractory curves slope toward the quartz apex until they intersect the eutectic axis, then they swing

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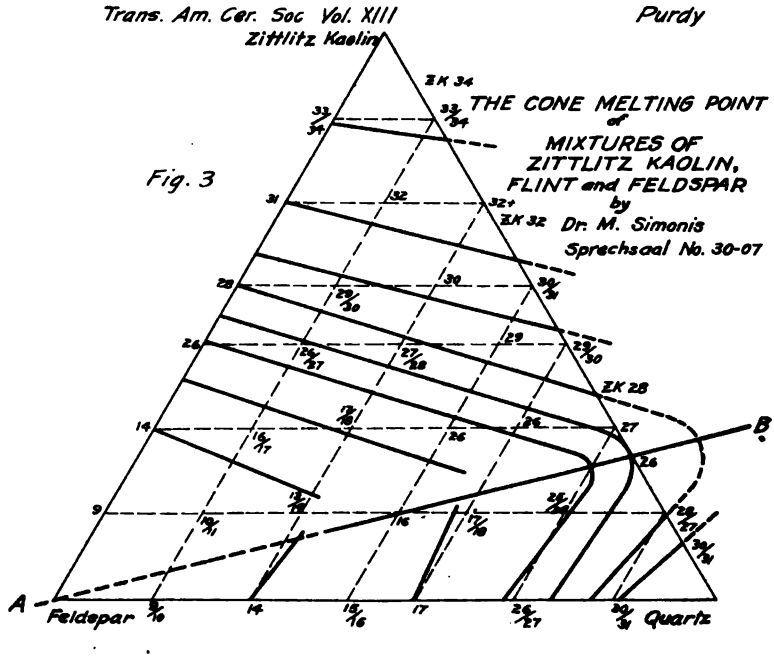
almost at right angles to their former direction. This is taken as evidence that in these mixtures we have two fluxes: (1) feldspar, (2) the clay-quartz eutectic. Simonies did not find a feldspar-quartz eutectic.



Work by Rieke.—In a similar way, I have drawn curves representing results obtained by Dr. R. Rieke and published in Sprechsaal, Nos. 15–17, '07 (Fig. 4).

In this case we have a eutectic area which extends from the Magnesite-Kaolin eutectic in a diagonal direction, being influenced in this by the kaolin-quartz and the $MgSiO_3$-quartz eutectics.

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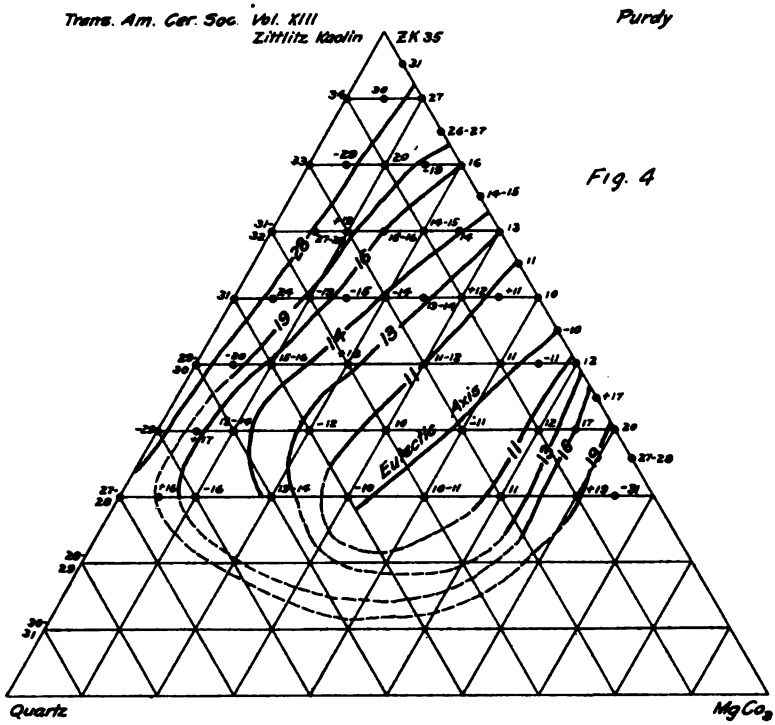

CONCLUSIONS.

From these two cases, and they are typical of others that are known, it is quite evident that the old idea of a flux is not sufficient to explain these eutectic axes. In the case of clay-feldspar-flint mixtures, feldspar is the primary flux, being aided in provoking solution by the clay-quartz eutectic, which serves as a secondary flux. In the case of magnesite-clay-quartz mixtures, none of the original components is the flux. In this, either the magnesite-clay or magnesite-quartz or possibly a eutectic between some magnesium, aluminun-silicate and $MgSiO_3$ is the real flux. If MgO was the flux, we would have had the eutectic axis projected from the $MgCO_3$ apex.

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In the same way it could be shown that in similar ceramic mixtures, calcium oxide is never the flux.

The flux in complicated silicate fusions is rarely a basic oxide.

We have had instances in our transactions where kaolin appeared to flux the mixture to which it was added, as, for instance, when added to a shale.[1] We have had numerous instances in which flint appeared to act as a flux. Seger, when making his experiments which led to the development of his pyrometric cone series, observed similar instances and commented on the fact that they were not in accord with the established notion of a flux. We have had several declarations to the effect "that evidently we will have to change our definition of the character and properties of flux and refractory substances."

Personally, I am not in sympathy with attempts to classify ceramic materials into fluxes and refractories, simply because the *fluxing action in a given mixture is a straight line proposition between the components involved only when the components form isomorphous mixtures.* In the large majority of cases, any component present in excess of that required to form a eutectic serves as a refractory constituent whether that constituent be basic or acid in character or whether when melted or fused alone it be easily fusible or refractory. How many of us can recall our surprise in not finding fluorspar an active "flux" in engobes and slips?

I argue for willingness to abandon old ideas whenever sufficient reason for doing so is advanced. I feel that we have in the past been wrong in our conception of fluxes and fusions and urge the adoption of that definition which will find the fewest conceptions. The definition for fusion given here is the same as the one so often given by physical chemists. The definition for fluxes is not new in the fundamental principle and conception but it is new in regard to limitations.

[1] Bleininger and Moore. Trans. A. C. S., Vol. XI. p. 332.

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Note Prepared after Having Read the Paper.

Mr. Kerr: I agree with Prof. Purdy in the stand he has taken in considering the action of fluxes in ceramic mixtures. Physical chemistry has made wonderful strides in the past decade, and in the future the results obtained by physical chemists promise to be even more epoch-making than any that have been obtained to date. The physical chemistry of the silicates is the most difficult part of the field, but some inroads have already been made and we have every reason to believe that the near future will bring forth results that will mark great advances in solving the riddles of ceramic chemistry.

Prof. Purdy has well pointed out studies in physical chemistry which have already been successfully completed, and which force us to abandon the idea we formerly held that a flux was a material which when added to a ceramic mixture, would set up a general attack upon the whole mixture and cause it to fuse at a lower temperature than would otherwise be required to bring about fusion. We must adopt the new idea consistent with the laws of physical chemistry that a flux is that part of a ceramic mixture which is the first to become liquid and which then dissolves or tends to dissolve those components which are present in excess. The flux is seldom any one of the original ingredients in the form in which it was added. Sometimes it is a compound formed by chemical reaction from the original ingredients. But in commercial ceramic bodies it is probable that practically all of the real fluxing constituents are eutectics formed between certain ones of the various components present. There usually are, of course, chemical reactions to be taken into account, but we are compelled to believe that the physical solution processes which occur with and follow the chemical reactions are the real fluxing phenomena.

There are many obstacles presented to the student of silicate chemistry, and probably the chief one of these is the extremely high viscosity of silicate melts. A fusion which is only change of viscosity must not be mistaken for an actual melting. Prof. Purdy has called attention to this.

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RANGE IN COMPOSITION OF GLAZED WHITE WARE BODIES MADE FROM CLAY, FELDSPAR AND FLINT.

By Ross C. Purdy, Columbus, Ohio.

White ware body compositions, in many writings, have been classified industrially on basis of their relative absorption without regard to their biscuit heat treatment. It is not necessary to give references to writings in which this basis of classification has been used for it is easy to prove that the arguments on which such a classification is based are far from being sound either technically or practically, but without discussing this question directly, I will briefly state the requirements in the principal white ware bodies before attempting to outline the proposed classification.

The industries using compounded white bodies of the type here experimented with, may be grouped as follows:

(*A*) Porcelain, china, belleek.

(*B*) General white ware and decorative ware.

(*C*) Majolica.

(*D*) Wall tile and dry pressed electrical insulators.

PORCELAIN CHINA AND BELLEEK.

(1) The "body" of wares known as porcelain, china and belleek is *vitrified* either in the bisque or glost fire.

(2) All china and belleek bodies must have a *high degree of translucency*, but for porcelain, this is important only in the finer pottery wares.

(3) The bodies used in manufacture of belleek and china and in porcelain pottery must permit of casting or jiggering into thin wares, and especially is this important in the manufacture of the type of belleek here referred to, *i. e.*, those made without a fritt as one of the body constituents.

(4) For all these wares, whether made thin or thick, the body should have low drying and burning shrinkage.

(5) For all wares of this group, the burned bodies must be free from color. For those used in manufacture

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of glazed porcelain of heavy construction, this requirement is the least imperative and for those used in china and belleek most imperative.

(6) With the exception of porcelain for floor tile, and finer china bodies for bas reliefs, these bodies are glazed. The porcelain are glazed with a mixture that is very similar in constitution to the body, but made more fusible by addition of whiting and zinc.

The china and belleek are glazed with a fritted lead boracic acid glaze which in most cases mature at cones ranging from 1 to 3.

The most essential difference between china and porcelain, aside from the glaze used, lies in the fact that porcelain are dipped either in the unburned condition, making what is termed "one-fire ware," or after having been biscuited at least four or more cones lower than the glost heat treatment and sometimes as low as cone 010, either of these procedures resulting in simultaneous maturing of glaze and body. In case of china and belleek, on the other hand, the biscuit heat is sufficient to mature the body (thoroughly vitrified), the biscuit then being covered with comparatively easily fusible fritted glaze at a heat treatment four or more cones lower than that of the biscuit.

These differences (*a*) in character or constitution of the glaze; (*b*) in degree of vitrification of biscuit prior to the application of the glaze; (*c*) in relative intensity of glost and biscuit heat treatment, demand the consideration of many factors and the study of data obtained with many glazed body combinations before limitations of area of body variations, characterized by "glaze fit," can be determined for each of the wares of this group. The area of "fit" obtained with china or C. C. bodies do not hold for porcelain where a different type of glaze is used.

Those bodies of the present investigation which were vitrified in the biscuit burn, and then glazed, may be considered as conforming to the practice prevailing in the manufacture of china and the frittless belleek.

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GENERAL WHITE WARE AND DECORATIVE WARE.

(1) The biscuit for these wares have an absorption ranging from 1 to 7 per cent. Most "general white ware" manufacturers in this country make "white granite" or "semi-porcelain," which approach, in most properties, to china. In white granite, the absorption of the biscuit is low (1 to 2 per cent.). In the heavier, cheap hotel and restaurant ware, known as "C. C.," the body is not so close, in its properties, to china. In these, the absorption runs high (7 per cent.). Biscuit for over-glaze decorated jardineers are made from bodies similar to C. C. biscuit.

(2) For white granite, the body should be naturally white or rendered white by the use of a cobalt stain. Color in C. C. body is not a matter of much consideration.

(3) In the manufacture of white granite (or semi-porcelain) the biscuit fire generally exceeds the glost heat-treatment by 2 to 4 cones. In the manufacture of C. C. ware, the biscuit and glost heat treatment are often identical.

(4) Fair translucency is required in white granite but not in the C. C. wares.

(5) The working properties of these bodies must be such as to permit the formation into wares by jiggering. Owing to the fact that the white granite bodies are made into thiner wares, they require more attention in this respect than do the C. C. bodies.

(6) Summarizing the requirements of bodies included in this group, we have:

Properties	White granite	C. C.
Vitrification.	1 to 3% absorption at cones 4 to 8.	2 to 7% absorption at cone 4.
Translucency.	Fair.	Not required.
Working properties.	Must be sufficiently plastic to jigger well and have sufficient bonding power to dry well.	
Shrinkage.	Should not exceed in total shrinkage 10%.	Total shrinkage not of importance.
Color.	Fair.	Not important.
Glazing.	Bodies for white granite require larger "Area of fit" than do the C. C. bodies.	

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MAJOLICA.

(1) In America, bodies used in majolica (ware covered with colored glazes) are quite similar to the C. C. bodies of the preceding group, in fact, the two groups overlap considerably. The majolica body can be more porous than any of the bodies previously considered.

(2) The biscuit heat treatment rarely, if ever, exceeds cone 4. Cone 1 or cone 2 is the most commonly practiced biscuit heat treatment.

(3) The glaze ordinarily used on this class of ware is known as "raw lead," fritted glazes being used only to obtain special color effects. With raw lead glaze, the burden of the responsibility in maintaining a large area of "fit," falls on the body composition, economic factory practice requiring that the body must be so constituted as to permit of a variety in types of glaze used.

(4) Inasmuch as the usual biscuit heat treatment is lower than that of C. C. ware, and, since the glazes used are varied in constitution, it is essential that none of the bodies should lie close to the boundary line of the "glaze fit" area obtained in this investigation.

WALL TILE.

The biscuit for wall tile has requirements that do not prevail in pottery industries. These requirements are:

(1) **Color.**—Must be uniform, *i. e.*, free from dark specks and discolorations, but need not be pure white. Cobalt stain is rarely, if ever, used to counteract the yellow tint produced by the iron and titanium in the materials used, for in dry pressing, the surface of the ware being rougher, the tints produced by these colorants are not so prominent as on the smooth surface of the plastic made wares.

(2) **Working Properties.**—Owing to the fact that wall tile is made by the dry press process, it does not require the plasticity or bonding power which is so essential in pottery bodies. For this reason the proportion of china to ball clay may be greater.

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(3) **Absorption.**—Wall tile can have greater porosity, *i. e.*, higher absorption, than any of the bodies so far considered, but it is better practice, however, to have as low absorption as possible. Most wall tile biscuit has an absorption of 5 to 10 per cent.

When the porosity is great, 15 per cent. or more, special glazes must be used. For example, the glaze used in these experiments when applied to a commercial wall tile having a large porosity, and burned in the gas kiln glost burn, did not mature, in fact, it apparently disappeared entirely from the surface of the tile (see A. C. S. Trans., Vol. II, p. 158).

Tile with high porosity does not possess special advantages in any way over those of low porosity. High porosity in itself has no advantage in the fitting of a glaze or in the adherence of the tile to cement. It has the disadvantage of giving opportunity for absorption and crystallization of salts from the cement, causing the glaze to craze.

Wall tile biscuit can have, all other things considered, an absorption as low as 6 or 8 per cent.

(4) **Warping.**—In the foregoing paragraph it was stated that "all other things considered," absorption for wall tile may be as low as 6 or 8 per cent. One of the most important things to be considered in this connection is buckling. Buckling in wall tile is the bowing up of the tile in the glost fire. The tile may be perfectly straight in the biscuit and yet buckle up considerably in the glost.

The exact cause of this specie of warping is not known. Sufficient evidence is at hand, however, to state that biscuit, high in feldspar (over 15 per cent.), are very apt to warp, in fact, tile containing only 10 per cent. feldspar have been known to warp. If the best proportion of flint and clay, and the best combination of clays, be used, the feldspar may and usually does amount to 15 per cent. of the batch, but, as a rule, the feldspar content should be kept as low as possible.

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If low porosity can be obtained with a heat treatment that is economically feasible, and with a content of feldspar low enough to avoid likelihood of warping, it would be more desirable than high porosity.

(5) **Glaze Fit.**—The wall tile body must lie well within the area of the fit for the glaze used. While much of the control of the extent of "area of fit" lies in the glaze, it is important that the body should be so constituted as to permit of the use of a large variety of glazes.

(6) **Strength.**—A wall tile biscuit made from feldspar, clay and flint may meet all the requirements so far as color, glaze fit, and minimum liability to warp are concerned and yet have so little strength as to cause heavy loss in shipping and laying. Feldspar bodies are notoriously weaker than Cornwall stone bodies, hence, in many of the American wall tile factories we find that Cornwall stone has largely replaced feldspar as the "body flux." These mixtures are not included in the present discussion.

LIMITS OF BODY COMPOSITION.

Pottery.—It is of interest to note that the white ware potter's old rule (which is adhered to quite closely in practice) is that the proportions of body ingredients can not vary widely from:

12 clay
9 flint
4 feldspar
—
25

This narrow range of possible body variation found in practice is caused by many factors other than glaze fit, as, for instance:

(*a*) Sufficient clay to give requisite working properties in the plastic, yet not enough to cause difficulty in filter-pressing or to cause excessive shrinkage.

(*b*) Feldspar content not so high as to cause warping and yet sufficient to cause the required degree of vitrification.

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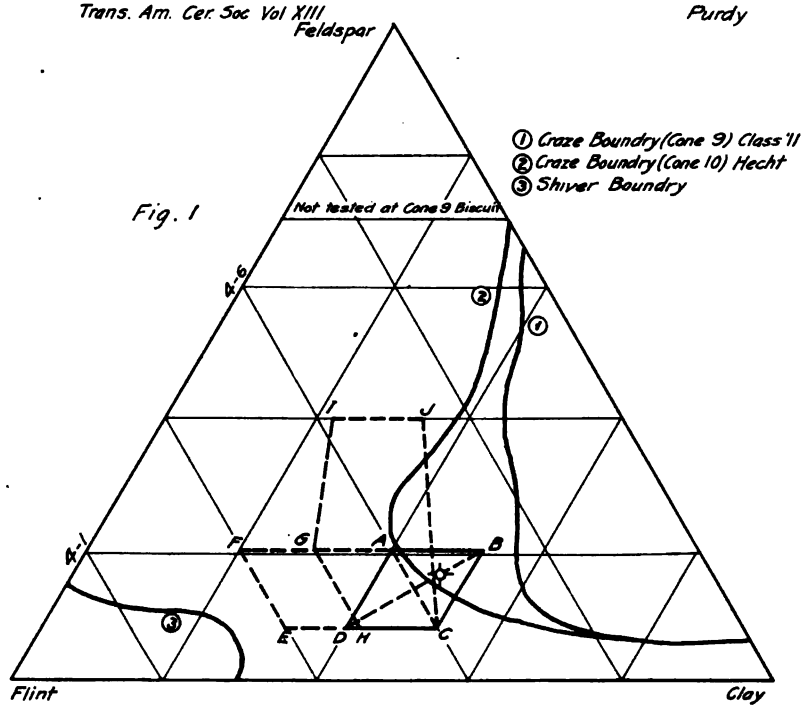
(*c*) Sufficient flint and china clay to give whiteness and surface texture. Since both feldspar and ball clay give color, effort should be made to have the contents of flint and china clay as high as possible.

With all of these limiting factors in mind, the parallelogram A, B, C, D, has been shown on Fig. 1 as indicating the practical range in body composition for white wares.



The sides AD and BC show the limit of clay content (40 ± to 52 ± %); the side AB and DC show the limit of feldspar content (8 ± to 20 ± %) while the length of the diagonal BD indicates the range of variation (52 — 30%) in flint which would follow as a consequence of the above variation in clay or feldspar. The point on this diagonal

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marked by a star corresponds to the body composition given in the potter's rule before quoted.

Since the corner B of the parallelogram lies close to the boundary between the fit and craze area as found by us and since it would lie within the craze area as determined separately by Hecht, Weelans, and Purdy with widely different body materials, glaze composition and firing conditions, etc., it is obvious that the bodies lying within the triangle ABC are more likely to craze, and will not be much more plastic and will not be as free from iron coloration as the bodies in the triangle ACD. The bodies in the triangle ACD would, therefore, be better for the plastic white ware manufacturing processes than would those in the triangle ABC.

Dry Press Ware.—For white wares made by dry press processes the considerations are somewhat different than for those made by plastic processes, and to adequately discuss the limits of variation in dry press white ware body compositions, these wares will be divided into two groups:

(*a*) Vitrified and of complicated design (electrical insulators).

(*b*) Not vitrified and of simple design (wall tile). All bodies lying within the parallelogram FACE (in dotted lines) would (so far as body composition is concerned) be free from glaze defects.

Bodies within the parallelogram GACD no doubt would be best for wares of the first group, such as electrical insulators of complicated design made by dry pressing. They contain sufficient clay to bond the mass when pressed and they lie safely within the "fit" area. They may not vitrify as easily as required under some factory conditions, hence, as a more vitreous area, we have I, J, C, H, G, in which the clay-flint ratios remain the same as before. In other words, area I, J, C, H, G results from addition of feldspar to the bodies in area G, A, C, H. On these higher feldspar bodies, however, it is customary to use glazes of the porcelain type rather than a fritted glaze.

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For the ware of the second group (wall tile), biscuit bodies within the triangle FCE are no doubt the best. Low feldspar to obviate buckling, and high flint to give whiteness and low shrinkage and just sufficient clay (mainly kaolin) to give the strength required for safe handling before biscuiting would be the features making these bodies desirable for wall tile.

CONCLUDING REMARKS.

(1) In the above discussions, attempt has been made to lay emphasis upon the fact that working properties, color, translucency and glaze fit under the several industrial conditions are *the* criteria upon which a classification of glazed white ware bodies must be based and that a classification based on relative absorption would not only lead one sadly astray, if required to produce a body for a given purpose, but would also include body mixtures that are utterly impossible under factory conditions.

(2) The above discussions lead also to the very obvious conclusion that the possible range in variation in the glazed white ware bodies are very narrow and that the difference in formulae used by the manufacturer lies more in the combination of brands of clays, feldspar and flint than in the total "clay" or feldspar content. This is shown to be true in experiments reported by Ernest Mayer (Trans. A. C. S., Vol. IV, p. 27). If a feldspar-clay-flint body formulae has a value for a given purpose or is cherished as a trade secret for any reason, that value would lie wholly in the kinds of materials used and the peculiar proportioning of the several kinds. One potter's china recipe contained nine clays, each in an odd proportion but that potter had reasons for the use of each of those clays, and for the proportional quantity of each, and valued his reasons at $1000.00. Yet when his formula was reduced to the simple terms of feldspar, clay and flint, it did not differ materially from that of his neighbor who was making an inferior ware.

(3) Having the best possible combination of materials it is still possible to make inferior wares, and poor crafts-

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manship need not necessarily be the cause. Proper biscuit and glost heat treatment, glaze composition and preparation are essential to success in any glazed white ware industry.

(4) Having defined one person's idea of the limits of body composition for the several glazed white ware industries, it is hoped that others will put their body formula in the simple terms of feldspar, clay and flint, thus aiding us to have in our transactions an accurate as well as a practical statement of the limits of possible variations in body composition.

DISCUSSION.

Mr. Parmelee: I should like to ask whether the flint, feldspar and clay, as shown on the figure, are the ordinary commercial materials, or do those terms represent the composite mineral constitution of the materials used?

Mr. Purdy: The clay, feldspar and flint, as indicated, were the commercial materials, no attempt being made to determine their mineral constitution.

Mr. Parmelee: What is your opinion regarding the effect of the variations in the clay composition?

Mr. Purdy: They would not materially alter the relative area of craze, fit, and shivering, and certainly not the limits of possible body variation for any particular kind of white ware product. A physical difference in the clays are just as apt to be effective in this respect.

Mr. Parmelee: Do these variations, as outlined by the parallelograms, represent compositions successful at definite cone temperatures, that is, in the triangle ABC, for instance, do they represent definite temperatures?

Mr. Purdy: We had separate bodies burned at definite heat limits. With the glaze used, the craze area was bounded by that line, and all the rest of it was fit, whether the biscuit was burned at cone 1 or cone 10. We know, however, that you must burn semi-china biscuit at cone 8 in order to get a good body. If another body mixture should require greater heat treatment, you must use a higher cone;

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and if less, a lower cone; all, however, must be confined in that triangle. I have taken several formulae for bodies I know to be in use, and reduced them to the simple terms of clay, feldspar and flint; and they all fall in these areas. The diagram is not based altogether on our experimental results in the laboratory.

Mr. Barringer: In the electrical porcelain area described, could not the flint be cut down considerably from a practical standpoint? For instance, I notice that your JIG triangle is well over the 40 per cent. clay line. We plotted an area something like that, and then deliberately drew 40 per cent. and 60 per cent. clay lines through it, and took the area between these clay lines as being the most practical.

Mr. Purdy: The extreme clay content in the area for electrical porcelain, shown on the diagram, is about 60 and 22 per cent.

Mr. Barringer: Well, if you run over 60 per cent., you are apt to have sticking to the molds in dry process porcelain, and under that, it does not keep its shape. Arbitrarily, therefore, we take between 40 per cent. and 60 per cent.

Mr. Purdy: I define as the area for your complicated electrical insulators as G-A-C-H, which has as limits in clay content 30 per cent. and 60 per cent.; but in simple designs, where you are using a feldspar glaze, you can project your bodies into the area GIJ. I know of three or four electrical porcelain plants using bodies located near the point J, but I have not heard of any using bodies located near the point I.

Mr. Barringer: I just spoke of that because I thought it was the outside limit. In the same way, to draw a practical limit on feldspar or flint would probably narrow your limits considerably for these ingredients.

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THE RELATION BETWEEN THE ARTIST AND THE CHEMIST IN CERAMIC MANUFACTURE.

By HERMAN C. MUELLER, Trenton, N. J.

A ceramic piece of work consists of burnt clay shaped into form to serve a certain purpose.

The production of a ceramic piece of work may therefore be divided into the preparation and manipulation of the material, and the work of bringing it into the desired form. The first part comprises the work of the chemist, while the second part is done by the artist. The co-operation of both brings the best results.

If a chemist strives to produce combinations of color and texture which may support the ideas of the artist, and if on the other hand, the artist will try to make the most out of the material developed by the chemist, and conceive fitting applications, the co-operation is perfect, and the results can only be satisfactory.

Each craft has limitations, and compromises are constantly asked for by each party engaged in co-operative work. It may be said that the work of the artist is by far the more pleasant of the two. He can always base his artistic-esthetic speculations on something tangible, on something which has already been developed as far as texture and color is concerned, and his work does not, therefore, include experimental uncertainties. He can feel perfectly sure that an object which he has in mind can be carried out without a hitch.

The chemist is not as sure of his ground, as his work consists of constant experimenting, which may or may not bring the expected results, and which often involves vexing disappointments.

The great difference in the work of the two crafts can easily be perceived in the great difference between the workers, and it is a well-known fact that artists and scientists have but seldom been close together. They do not mix well, and to be plain about it, it may be said that they sometimes show a little contempt for each other.

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There have been men engaged in the production of pottery who combined practically all necessary knowledge, who were well acquainted with the material and who had a fine feeling for form and decoration. These men, however, were exceptional at all times, and in our era of specialization they become scarcer all the time, so that we may take the division of the work as an accomplished fact and try to make the best of it.

Nearly all Ceramic Societies have been started and developed by the modern scientifically trained members of our craft, and the great service that these men have done our clay industries cannot be over-estimated. It is also easy to understand why these men came so readily together. Their training made them comrades from the very beginning, and as the technical problems are practically the same throughout the whole industry, a constant interchange of opinion and a desire to compare experiences made the formation of a Society an easy matter.

The artists engaged in pottery work have, as a rule, not been very prominent as members of the Ceramic Societies. This statement may apply to the Ceramic Societies of the world.

This is not as it should be. If artists and chemists can and must co-operate in their daily work, they might as well co-operate in their deliberations as a group. There are many reasons given for the aloofness of the artists. They lack, as a rule, the literary knowledge which the scientist possesses. Their work cannot be explained as readily as the work of the chemist, and consequently they feel that they are occupying the humiliating part of "fifth wheel" in the deliberations of the Ceramic Societies, especially as they cannot participate in the discussions about the combination of materials, and the various scientific problems presented in the meetings. They furthermore assert that considerations of form and decoration are seldom, if ever, touched during the meetings.

We must admit that there is some truth in these statements, and we must also admit that it would be well if

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Ceramic Societies would embrace all intelligent elements of the craft. As stated at the beginning, the ceramic art embraces matter and form, and the Ceramic Society which would unite the co-workers would naturally become stronger than a Society which only embraced certain specialties.

If the work of the chemist is benefited by mutual intercourse, the work of the artist must also be improved, and I should think that it would be in interest of the manufacturers to assist the Ceramic Societies by inducing their artists to become active members. To find and provide a place in the Association, by perhaps starting a separate section, which again might be subdivided, would perhaps solve the problem.

Artists are, as a rule, valuable acquisitions to any society, for various reasons, and I may be permitted to express the hope that your Society will take this matter up sooner or later, for serious consideration.

The clay industry of the United States has become a very important factor, and your Society has done meritorious work in more than one direction. It has acted as a pioneer in a technical direction, establishing the fact that the clay worker cannot depend any more upon the so-called practical workmen alone; that the old "thumb-rule" is entirely too uncertain and antiquated for modern manufacture.

While, therefore, the technical part of our work is rapidly developing, the same cannot be said of the artistic part, especially in consideration of our ordinary pottery. We have a few art potteries in the United States which are doing great work, but the potteries of utility ware are sadly lacking in ambition, as far as form and decoration are concerned. Many potteries which could well afford it either purchase their blocks and models from abroad, or simply use the same model over and over again.

I feel sure that your society can do a great deal to help artistic development by making an effort to interest manufacturers and artists in its endeavors, and by constantly calling attention to the fact that nearly all clay work depends on its decorative qualities.

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Statistics show that a great amount of artistic pottery ware is constantly imported from Europe, and unless we exert ourselves to develop the artistic merit of our own work in our own way, and according to our own taste, we can never hope to raise our clay industry to the same artistic level it has attained in Europe.

The desire to grow in this direction is manifest. Industrial Art Schools are established in various parts of the country, and the general public shows its awakening interest in the higher technical and artistic training of our workmen. The manufacturers, however, who play the most conspicuous part in this direction in Europe, do not show the desired ambition in this country, and many of them think that artistic work does not pay.

It will not pay as long as we have to draw on Europe for artistic skill, but as soon as we are able to develop our own artisans and artists, it will surely pay every one concerned.

Expressing the wish that my suggestions may meet with your favorable consideration, I will close with a hearty wish for the prosperity of your estimable society.

DISCUSSION.

Mr. Binns: There is a good deal of truth in what Mr. Mueller says, yet when you analyze the question, you are forced to one of several conclusions. I do not know of any occasion, in any part of the world, on which artists come together to discuss subjects of this kind from the artistic standpoint. There are exhibitions of paintings and there are art schools, but where do you have a society of artists who come together to discuss the matters of technique? The fact is, it would be a practical impossibility to secure agreement among artists. The artist is a man who is sure of himself, hence, naturally impatient of the expressions of opinion on the part of another man.

There is another thing to be considered. Suppose that one of us were to discuss an art subject. Such a subject is worth nothing without illustrations. For this purpose, he might bring his own work, and then he would

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lay himself open to the charge of self-glorification, and if he should bring the work of some one else, he would lay himself open to the charge of envy. We are between the devil and the deep sea. Busy as we are, it would be difficult to give such a subject the attention that it deserves. I think that it would be a nice thing if we could have, in an impersonal way, something of this kind to discuss, but an impersonal discussion would be a difficult thing to secure. We must have either our own or others' products to illustrate our remarks.

Moreover, our Transactions are now as full as they can be made, and it is all that we can do to handle the things as they come. The real remedy, I think, is in the personal endeavor of each member of the Society to improve his own product, if he has one, in this direction. In this connection, I may add that our efforts in the direction of improving quality in body are as truly artistic as any in regard to improvement in design or drawing.

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REPORT OF THE COMMITTEE ON CLASSIFICATION OF WHITE WARE.

By CHARLES WEELANS, Chairman, and HARRISON E. ASHLEY.

Mr. President: Our Committee is able at this time to make only a partial report.

Considerable work has been done, principally by our late friend and member, Mr. H. E. Ashley. The Committee realizes that they have lost its most valued member, and owing to this our report is not what it might have been.

We set out to test all the different lines of white ware manufactured in the United States, and, for comparison a number of the wares manufactured in foreign countries.

Our tests comprised the following:

Body test	Porosity and bulk specific gravity (immersion).
	Translucency (sieve).
	Vitrification (red ink).
Glaze test	Craze.
	Hardness or toughness.

Our plan was to secure from each manufacturer a sample of the hardest and a sample of the lighter fired ware, the object of this being to arrive at a fair average of each class of product, and to determine, if possible, a standard of merit within the possibility of attainment on the part of each manufacturer, and still be of such character as to permit of its acceptance after rigid examination on the part of the users.

In our efforts to secure samples for testing we have met with pronounced courtesy from the various manufacturers, but a lack of desire on their part to furnish other than the best samples of their product was noticeable.

We consider this, however, a mistake, for should we establish a standard secured by a test of their best samples only, it is evident that the run of ware would not be successful in meeting that test.

We think, therefore, when our aim and purpose is better understood there will be no hesitancy on the part

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of the different manufacturers to furnish not only their *best* but their *worst* samples and in this way facilitate the work, the result of which would be much more satisfactory to all.

We had hoped, in the course of our work, to also establish these various tests of quality, making them simple and easily applied by any one at any and all points of destination, if desired.

Dispite the amount of work already done by our Committee, we are yet unprepared to give a satisfactory and complete report, but should the Society think fit to continue it, in all probability by our next meeting a more complete result might be looked for.

Mr. Hurst will kindly explain in detail just what has been accomplished thus far and pass among the members of Mr. Ashley's absorption test, explaining the composition of the stain used.

DATA ON WHITE WARE TEST.[1]

It was proposed by Mr. Ashley to make the following tests on the white ware samples collected by the committee. Such data as was obtained in the partially completed work is given below.

Red Ink Test.—Bits of each sample were thoroughly dried and immersed in a red ink solution for eighteen hours. The depth of penetration was noted and the samples ranked according to their absorption. The results of the test appear in Table 1. The ink solution used was made up of

5 gms. Eosine (Tetraiodofluorescein).
25 cc. Ammonia.
475 cc. Water.

ABSORPTION, POROSITY, SPECIFIC GRAVITY.

Samples were dried thoroughly at 100° C., weighed, placed in a vacuum jar and exhausted till a vacuum of about 28 inches of mercury was obtained. Water was admitted

[1] Prepared by Ralph K. Hursh by permission of the Director, Bureau of Standards.

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to cover the pieces and they were boiled in vacuum for about 5 hours. The wet and suspended weights were then made and the per cent. absorption by weight, the porosity, bulk and apparent specific gravity were calculated.

$$\% \text{ Absorption} = \frac{W - D}{D} \times 100$$

$$\% \text{ Porosity} = \frac{W - D}{W - S} \times 100$$

$$\text{Bulk} = \frac{D}{W - S}$$

$$\text{Apparent specific gravity} = \frac{D}{D - S}$$

W = Wet weight
D = Dry weight
S = Weight suspended in water.

TABLE I.

Red Ink Test.

Rank in ink test.	Depth penetration. mm.	
1	0	Edges not colored,
2	0	Edges very slightly tinted,
3	0	Broken edges very slightly tinted,
4	0	Broken edges slightly tinted,
5	0	Broken edges slightly tinted,
6	0	Broken edges slightly tinted,
7	0	Broken edges slightly tinted,
8	0	Edges clearly tinted,
9	0	Edges strongly tinted,
10	2	Edges strongly tinted,
11	5	
12	15	Less readily colored near glazed surface,
13	7	Layer 0.4 mm. thick next glaze, wholly colored,
14		
15		
16		Wholly colored, all practically alike.
17		
18		

TRANSLUCENCY.

The object in this test was not to obtain accurate photometric measurements but to determine the

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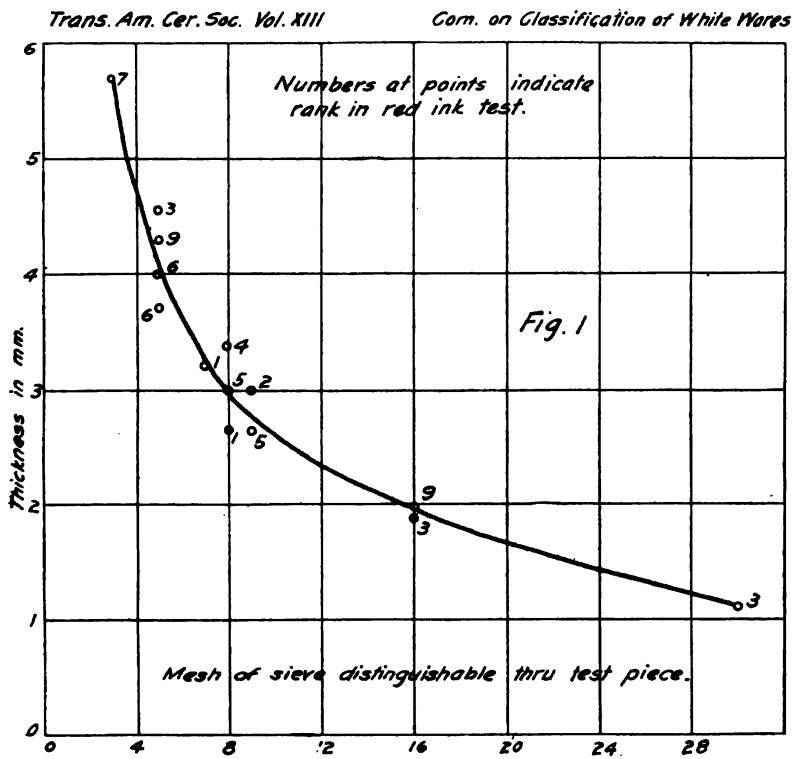
relative translucency of the specimens by means of a simple test which could easily be duplicated. After trying several devices a series of screens was used in which the diameter was about 1/4 the mesh. These screens were placed at a distance of about 3 inches from an incandescent electric light with a reflector and the whiteware samples held flat against the wires. The smallest mesh distinguishable through a specimen was noted and the thickness of the piece measured. The curve in Fig. 1 shows the relation of the translucency determinations to the thickness of the specimen and indicates that this translucency is inversely proportional to the thickness.

For this test a standard series of screens with regular



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variations of size and a constant ratio in the diameter of the wire and width of opening might be adopted and used with a lamp of standard intensity.

TABLE II.

Rank in ink test.	Per cent. absorption.	Per cent. porosity.	Bulk.	Appar. sp gr.	Translucency. Mesh.	Thickness. Mm.	
1	0	0	2.254	2.254	6–8	3.21	
1					8	2.65	
2	0	0	2.306	2.306	8–10	3.00	
3	0	0	2.314	20314	20–40	1.10	
3					12–20	1.90	
3					4–6	4.55	
4	0	0	2.340	2.340	8	3.35	
5	0.030	0.071	2.345	2.345	8	3.00	
5					8–10	2.65	
6	0.031	0.075	2.393	2.393	4–6	3.70	Bisque.
6	0.018	0.041	2.220	2.220	4–6	4.00	Glazed.
7	0.014	0.032	2.375	2.375	2–4	5.70	
8	0.028	0.067	2.353	2.354	...	2.00	Translucent.
9	0.459	1.157	2.518	2.546	12–20	1.95	
9					4–6	4.30	
10	2.096	4.755	2.270	2.383			
11	2.295	5.266	2.295	2.422			Stony, approaching conchoidal fracture.
11							
12	4.192	9.050	2.159	2.373			Stony fracture; large pores.
13	4.544	9.900	2.177	2.418			Stony fracture.
14	6.718	14.800	2.196	2.577			
15	8.130	17.430	2.143	2.590			
16	8.673	18.540	2.174	2.625			
17	9.878	20.570	2.083	2.625			
18	12.450	24.660	1.980	2.630			

CRAZING TEST.

It was proposed to subject the specimens to alternate soaking in a hot solution of a salt and drying out in open air. This work had not been commenced.

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COLOR DETERMINATION.

This part of the work was turned over to Dr. P. G. Nutting, of the Bureau of Standards at Washington, for editing and will be reported by him.

HARDNESS TESTS.

Flat pieces were to be exposed to a sand blast test for the hardness determinations. The work on this had not been begun.

DISCUSSION.

Mr. Barringer: We place different limits in allowable percentage absorption on electrical insulators made by the wet and the dry process. This has some practical advantages. For instance, we know where to draw the line that marks the difference between a good and a poor insulator. In the same way, by classifying white wares and studying them, it might be possible to differentiate wares of one character from those of another.

Mr. Binns: This report is of extreme value to us all. It has just been suggested to me to ask the object of the investigation. What is this classification referred to?

Mr. Stover: The question had been raised as to where the line should be drawn between C. C. ware, white granite ware, semi-porcelain, and china. This caused us to make some investigation, that we might make a definition of one or the other kind of ware. I do not know that any commercial value was attached to the idea. It was more for the purpose of actually setting the limit. If the Committee's work does not in some way assist the man who runs a pottery, I cannot see that we have any particular reason to continue the investigation.

Mr. Orton: Since this matter was brought up for discussion a year ago, an incident has come to pass that shows how such a report could be used, if it were available. Some months ago I received an inquiry from an agent representing the Railroad Freight Classification Bureau asking me to indicate to him the proper classification

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for freight purposes of the pottery products offered for transportation and giving me the classification then in use. Not having spent very much time in recent years on this phase of ceramic work, I hesitated to state an opinion, but as the matter was one of importance, and it had been brought before me as the representative of the American Ceramic Society, an organization which he thought should be competent to frame an answer, I wrote him that I would undertake to obtain the sentiment of some of the members of the Society. I then wrote a circular letter to seven representative men in the organization, stating the facts, and putting before them all the information that had been given to me, and asking them to criticize the document which I had drawn up representing my own views, or rather, my notion of a basis of argument. Replies came in in due course of time, and it was found that scarcely any of the writers agreed with me or with one another. Seven answers gave seven different sets of ideas on the subject. Being unable to harmonize their views into a coherent whole. I modified my own statement by what seemed the strongest suggestions that had been made and sent this modified document to my distinguished colleague, Professor Purdy, and asked him for his views on the point.

Having read the document over, he got out several samples of different kinds of wares from our museum cases, and put them on the table. He then called up several men from the laboratory, who should have been at least more competent to form a judgment of the points involved than an ordinary freight agent, and asked them to classify these wares according to the proposed schedule. They could not classify them sharply or determine unanimously where any of the various pieces fell, and the document was returned with that answer.

Here is the situation: The railroads want to determine how they are to classify wares. They needed technical assistance, and came to this Society for it; and I do not think they got very much help. The question is, in the

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first place: Is the Society able to assist them, and, secondly, does it want to assist them?

Mr. Weelans: I should like to cast a little further light upon why this work of classification was first entertained. Certain dealers and consumers insist upon certain tests being applied to ware before acceptance. Some of these tests are beyond the manufacturer's ability to meet successfully. The object of this committee's work was to determine the tests which should be applied to each separate ware according to its kind, and to classify the white wares and specify the tests which should be used as a basis of standardization of such a classification.

Mr. Purdy: If we are attempting to lay down a basis for railroad classification, that is one proposition; if we are trying to distinguish between different kinds of pottery, so that the manufacturer may know whether for instance, he is making C. C. ware or china, that is another; and if we are endeavoring to develop tests for relative translucency, etc., that is still another. A railroad classification would not settle a dispute between two potters as to which one is making china and which C. C. ware, nor would a railroad classification be based upon a red-ink test or on a difference in translucency.

There is a phase of the work that should be taken up, and that is a study of the Government requirements for different wares. Are the specifications too rigid in some cases, as in sanitary ware? And, should the bars be let down to some extent? Are the government specifications on the right basis? If we can find anything wrong with the specifications used by the Government, which are now in print, we have a definite point to take up; but until the parties interested can show that the Government has made incorrect specifications, the Committee has no further work to do beyond that of developing scientific tests.

I wish to move that a vote of thanks be given to the Committee who have so far carried on this work, and that they be requested to continue their work in the develop-

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ment of the tests—not with any wish to standardize ware, but for the development of the tests *per se*.

Mr. Burt: I second that motion of Mr. Purdy's. It seems to me that there is a mass of good matter that the Society is anxious to get. I do not believe that the manufacturers, as a whole, are afraid of the railroads. I do not see where that would develop into any great difficulty. The point made by Mr. Purdy is, however, a very good one—that we should get at this specification in our various materials. It is true, not only in white ware, but also in any others. We ought to have a certain specification. Demands coming from the architects and dealers are more and more urgent for quality. At the same time, there is a certain limit beyond which a manufacturer should not be forced to go. We should draw the line, and, as a Society, we could set the standard, and say that we approve of such and such quality. If we can do that, let us try to do it. Then, if his ware is up to that standard, the manufacturer can go before the architects and say: "There is the standard, and I have reached it." If we can, through this Committee, develop this subject, I think that it would be a great shame to lose the chance; and I second Professor Purdy's motion sincerely. (Motion carried.)

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THE MEASUREMENT OF COLOR OF WHITE WARE AND WHITE WARE MATERIALS.[1]

By HARRISON E. ASHLEY.

White wares differ in color in either hue or shade or both. *Hue* refers to the *quality*, *shade* or tint to the *quantity* of light reflected from the ware. Thus we have buff, gray, slate, etc., hues each in various shades up to pure white and reflecting 50, 60, 70 per cent. of the light reflected by the pure white. The determination and the specification of the pure color must then ultimately be in terms of the relative quality and intensity of the light reflected from the specimen.

In theory, the color of white ware should be determined by comparing the light reflected from it with the light falling upon it, a spectrophotometer being used to spread a sample of each light out into spectrum and to measure the relative intensities of these spectra at each point. In practice, this method gives spectra too faint for the determinations of high precision necessary.

In practice, the eye can just detect differences in light intensity of about 1 1/2 per cent. Samples differing by less than that amount in reflecting power are in effect of the same shade. This photometric sensibility (1.5+) is further independent of intensity over a wide range of moderate intensities (Fechner's Law), practically independent of color (König's Law) and is the same for white and for monochromatic light. The uncertainty in a series of photometric reading is from 0.5 to 0.7 per cent., roughly half the photometric sensibility.

In determining the colors of unknown whitewares, no method can excel in sensibility or ease the direct comparison with a graduated series of standard samples, all of the same hue. The chief objection to this method is that the standard samples cannot be accurately reproduced nor

[1] This paper was prepared for publication by P. G. Nutting from notes and an outline of the intended paper prepared by the author shortly before his death.

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even copied with desirable precision. Their reflecting powers (shades) may be determined to about 1/2 per cent.

The use of *three color instruments* for determining both hue and shade has been proposed. The Ives "Universal Colorimeter" is of this type.[1] Light from three slits, covered with red, blue and green screens, is mixed in varied proportions until a match with the unknown sample is secured. Three scales give the proportions of light of each color used to secure a match. This instrument is not sufficiently sensitive or precise for determining the barely perceptible differences in hue and shade occurring in ceramics.

Single Color Standards.—In the Lovibond "Tintometer,"[2] the adjustments of color are made by adding successive colored glasses to the tube of the instrument. These glasses are empirically made in steps corresponding to the least color differences that the eye is able to perceive. Their value, like that of the Seger cones for heat measurement, depends on careful manufacture and accurate standardization. They are reference points, not absolute measures of light. G. A. Kerr[3] states that, when used by different members of the American Leather Chemists' Association, it gave very discrepant results. This may have been due in part to the lack of skill in securing a proper white light for the comparisons. As the instrument is adapted to give sharp readings for very delicate shades, it is much more promising for ceramic purposes than the Ives apparatus.

Ashley's[4] color standards, prepared by making various mixtures of light and dark clay, supply a method of proved value for pottery purposes, but with certain disadvantages.

He found it necessary to make a gray series for ball clays, and a buff series for china clays. A pink series for certain of the china clays would have made the compari-

[1] See Chem. Abs., 1, 2963; 2, 610.

[2] Pottery Gazette, 65, pp. 1269–71, 1910; also Joseph W. Lovibond, An Introduction to the Study of Color Phenomena.

[3] J. Am. Leather Chem. Assoc., 4, pp. 1–9; Chem. Abs., 4, p. 526, 1910.

[4] Trans. Am. Ceramic Society, 9, p. 56, 1907.

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sons less difficult. These standards were not suitable for measuring the color of whiteware bodies (greenish or bluish tinted).

As all commercial clays vary in color, a large quantity of standards should be made up at one time, if standard were to be generally adopted. In order to keep such standards clean, it is necessary to glaze them. Each glaze superimposes its own color (shade) upon the clay standard, so that the same clay base glazed at different potteries would not have the same values. Hence for valuing clays, each pottery should apply its own glaze to the standards and to the clays tested (assuming that it keeps its glaze composition always the same). But for comparing products, all the standards should have the same glaze.

A further disadvantage of glazed standards is crazing. This will apparently darken the piece, and so lead to false indications. It cannot be well avoided in a series of clay standards.

These considerations make it appear unfeasible for a central bureau to prepare and issue clay color standards.

An alternative is for manufacturers to prepare such color standards as best suit their materials and submit them for standardization.

Dr. Nutting has investigated the possibility of this by measurements upon Ashley's gray and buff color series, using the Marten's photometer[1] (see Fig. 1).

The results are given in terms of the whitest clay in the color standards, taken as 100, and total darkness, taken as 0, and give not color, but shade. Fig. 1 shows the total variations in the readings made (read as angles through which a prism is rotated), hence the extreme possible error. Dr. Nutting is having made a modification of the Marten instrument, with which it will be possible considerably to reduce the error of duplicate readings.

[1] Sold by Franz Schmidt and Haensch, Berlin, described in Verh. d. d. Phys. Ges' pp. 204–208, 1899.

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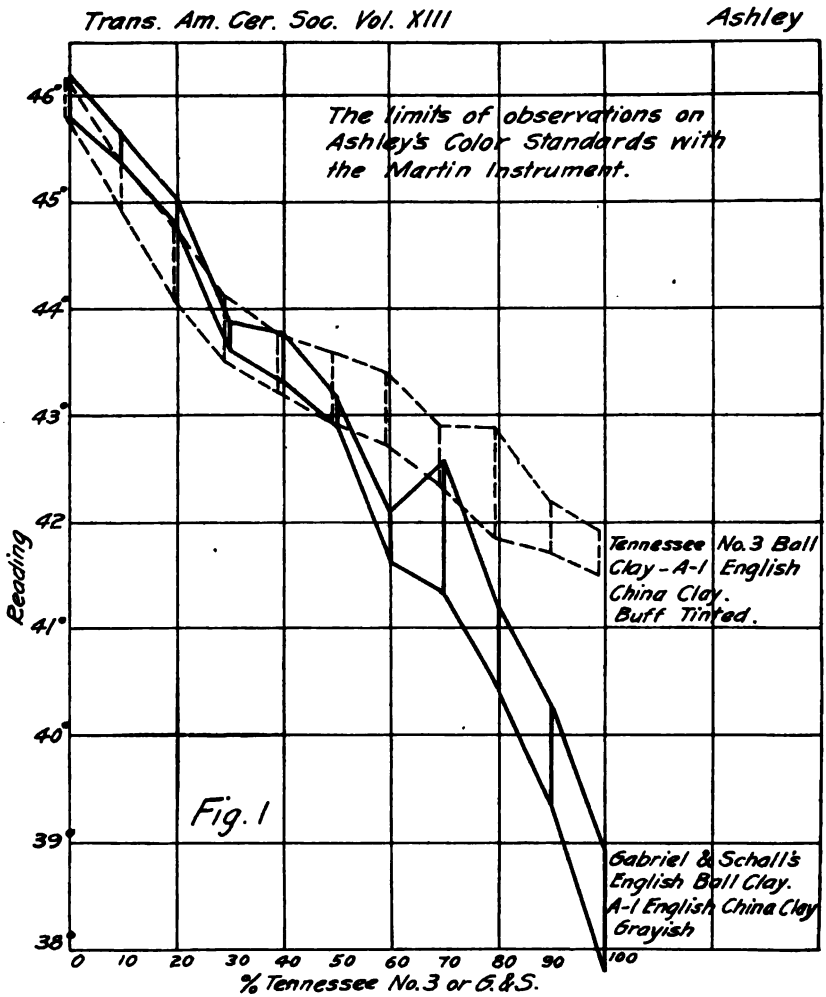

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TABLE I.

Relative diffuse reflection from two sets of Ashley ceramic shade standards.

"A1" mixed with "Tenn. 3."			"A1" mixed with "G & S."		
100% A I,	0% Tenn.	100% Refl.	100% A I,	0% G & S	100% Refl.
90% A I,	10% Tenn.	94% Red.	90% A I,	10% G & S	96% Refl.
80% A I,	20% Tenn.	89% Refl.	80% A I,	20% G & S	93% Refl.
70% A I,	30% Tenn.	86% Refl.	70% A I,	30% G & S	85% Red.
60% A I,	40% Tenn.	84% Refl.	60% A I,	40% G & S	83% Refl.
50% A I,	50% Tenn,	82% Refl.	50% A I,	50% G & S	81% Refl.
40% A I,	60% Tenn.	81% Refl.	40% A I,	60% G & S	76% Refl.
30% A I,	70% Tenn.	79% Refl.	30% A I,	70% G & S	75% Refl.
20% A I,	80% Tenn.	77% Refl.	20% A I,	80% G & S	69% Refl.
10% A I,	90% Tenn.	75% Refl.	10% A I,	90% G & S	64% Refl.
0% A I,	100% Tenn.	74% Refl.	0% A I,	100% G & S	58% Refl.

Dr. Nutting has also measured the shade of the samples of whiteware collected by Mr. Weelans, with the following results:

		Coefficient of diffuse reflection, relative to Ashley 100 A1 standard white.
1	Balleek, Lenox-Trenton	0.82 ± 0.02
2	Japanese China	0.68 ± 0.02
3	German China	0.79 ± 0.02
4	French Field Haveland	0.86 ± 0.02
5	Bone China, Trenton Pottery Co	0.91 ± 0.02
6	Bone China, Lenox–Tenton	0.92 ± 0.02
7	China, Mayer	0.74 ± 0.02
8	Lamberton China, Maddock Pottery Co	0.73 ± 0.02
9	Vitreous Lavatory, Thos. Maddock & Sons Co.	0.85 ± 0.02
10	Vitreous China, Cook Pottery Co	0.77 ± 0.02
11	Hard Vitreous, Mott	0.80 ± 0.02
12	Regular Vitreous, J. K. Mott Co	0.79 ± 0.02
13	Regular Vitreous, Trenton Pottery Co	0.68 (Sample unsatisfactory)
14	Soft Vitreous, Mott	0.86 (Sample unsatisfactory)
15	Semi Vitreous, J. L. Mott Co	0.85 (Sample unsatisfactory)

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16	Semi Vitreous, Trenton Pottery Co.....	0.95 (Sample unsatisfactory)
17	Semi Vitreous, N. Y. Pottery Co.....	0.89 ± 2.02
18	Semi Porcelain, Homer Laughlin.....	0.93 ± 2.02
19	Earthen ware, Anchor Pottery.....	0.87 ± 2.02
20	Earthen ware, Cook Pottery Co.....	0.84 ± 2.02
21	Earthen ware, Mercer Pottery Co.....	0.88 ± 2.02
22	Ironstone, Anchor Pottery Co.....	0.88 ± 2.02

The results of this comparison of color measurements are tentative. Promise is given by the Lovibond instrument, as a series of reference points, suitable for future more accurate designation, as the Seger cones are now repeatedly standardized with each advance in high temperature measurements. Or the Marten instrument will probably serve satisfactorily to standardize works clay standards in terms that will be comparable from place to place, whatever the composition of clay and glaze employed.

These observations indicate that a graduated series of reference shade standards can be prepared with sufficiently small and uniform steps for practical purposes, simply by careful mixing in definite proportions. They indicate further, the possibility of the direct calibration in reflecting power of such a graduated series of standards with sufficient precision for checking any one series or comparing one series with another.

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A METHOD OF CHARTING HEAT DISTRIBUTION IN KILNS.

By WILLIAM CANNAN, JR., Syracuse, N. Y.

Potters are learning to use "blind" as well as "sight" cones in order that they may know more about the distribution of heat in their kilns. Formerly they used only such cones as were so placed as to be in sight at all times during the burning, but since the Seger cones are recorders only of the heat treatment effect to which they themselves are subjected; and since, to be in sight, they are liable to drafts or air currents to which the saggered wares are not subjected; and since these cones record time-temperature effect, a flame may, in a short time, cause a deformation of the sight cones that would not be commensurate with the heat treatment which the saggered ware receives, it is not surprising that sight cones are not always reliable indicators of the heat treatment which is given to the ware. Having found this condition of affairs, we placed cones in the saggers with the ware, making what we called "blind" cones, *i. e.*, they could not be seen during the burning. These facts are not any more disparaging to the cone system of judging heat treatment than to the old Albany slip color trial, for both are rendered unreliable by the accidental as well as the consequential flame and draft effects.

We can all recall the surprises of finding a bad or a good burn when, from the sight cones, we had expected just the opposite. Such instances are common experience. The cones on the inside of the sagger in general show less heat treatment than do those on the outside, but it often happens that the heat treatment (as registered by the cones) on the inside and outside of the saggers are identical

There are so many factors that effect uneven distribution that it is not always possible in a given case to determine what may have been the cause of these irregularities. Length of flame from a given coal is as inconstant a factor as is the pressure on natural gas lines, and variation in length of flame is a very powerful factor in production of unequal heat distribution. Since length of flame is pro-

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portional to the volatile carbon in coals, and since the content of volatile carbon in coals is altered by weathering, we have in the fuel itself a factor which may be a considerable cause for these variations. Draft conditions, the condition of the heat gathering and circle flues, and that of the wheel and well hole, as well as the tightness of the bags, are important in this connection. Uniformity in the scotching of the bungs not only in the same setting but from time to time is important, and especially is this true in the first ring. These causes, and others, are to a great extent beyond the control of the burner.

By studying the conditions attending each kiln, and careful attention to regularity in baiting, a fireman may, to a large extent, become master of these situations. Before he becomes a master of these situations, however, he must have records of results obtained under the different firing conditions and it is on this that I wish to especially draw your attention.

To go blindly on without records of firing conditions, heat distribution, and character of results, would be equivalent to making no attempt to become a good fireman or to reduce the percentage of loss of ware or of cost of burning. Successful recording draft gauges, pyrometers, hydrometers and barometers are now on the market so that one can readily obtain records of all the conditions, aside from that of the character of the fuel and of the heat distribution. The fuel question is one that should be studied. I am simply offering here a method whereby we studied the one phase of this kiln problem, *i. e.*, heat distribution.

In Fig. 1 is shown a sample of the chart system we adopted for recording the heat distribution as shown by the sight and blind cones.

This chart represents a vertical section of the inside of a kiln. At the bottom of the chart a space may be provided for recording the condition of the ware, amount of fuel used and such other notes as concerns a history of the conditions and results attending a particular firing.

We had small prints made representing seven differ-

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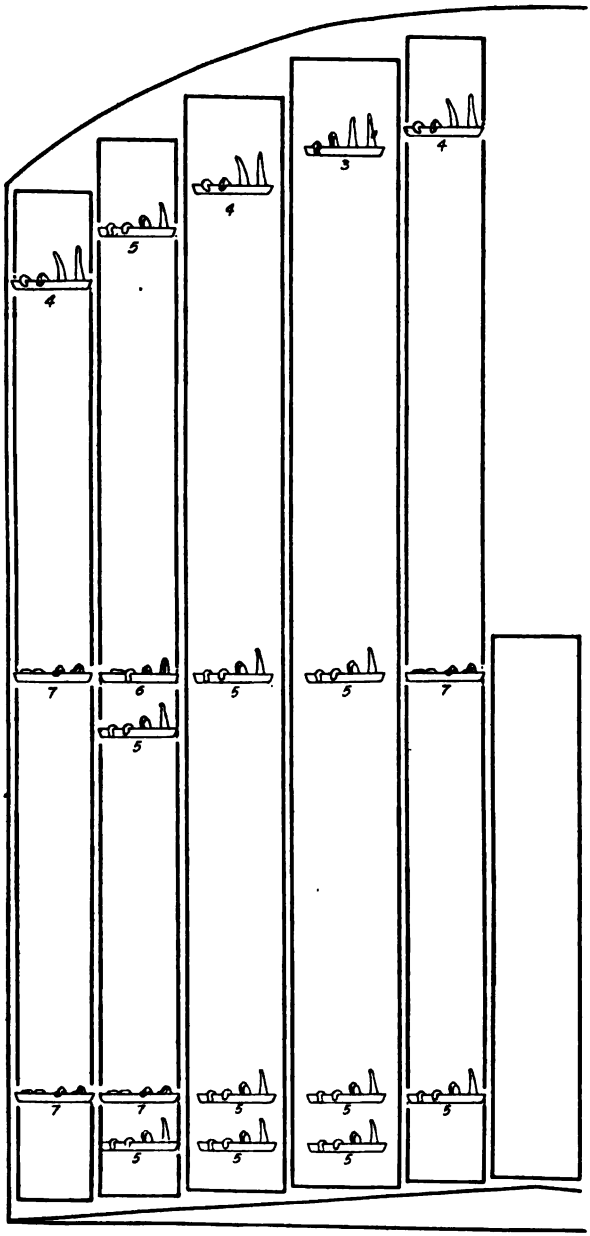

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ent stages in deformation of the four cones we used on each of the cone plaques. These prints were made on gummed paper so that the fireman could stick the appropriate one in the several places on these charts.

These cone prints were made in different colors, one color for sight cones and another for blind cones.

We have had this system of kiln records in operation since 1909 and consider these as important as a record of our business transactions. As a result of this detailed study of our firing conditions, we have not only greatly decreased our losses but have made our burnings so even in heat distribution as to considerably extend the setting limits for the more delicate underglaze colors. In fact, we are now not afraid to set wares decorated with fine lines in chestnut-brown the full height of the kiln around the well hole.

DISCUSSION.

Mr. Burt: As I understand, Mr Cannan, you make this chart, and give the kiln-burner the chart of the previous firing. We give the man a running chart, so that he cannot only have the chart of his previous burn, but also that of the one he is making, hour by hour. We give him the pyrometer with it, so that he may know each hour what he has had the previous hour.

One question that I want to ask Mr. Cannan is: "What method does he use in determining which biscuit is short and which is note. Is it merely off-hand judgment, or did you develop a test to tell by?

Mr. Cannan: The fireman jots down the peculiarities of the firing of the kiln so that the next time he fires that kiln he will have a note of what has happened with it before. We fire whole kilns of underglaze decorated ware, and have chestnut-brown decorations around in the fourth ring. If this can be done, the kilns are under pretty good control.

Mr. W. D. Gates: I appreciate the necessity of that even though we have not had a self-recording pyrometer. There

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is difficulty in getting a pyrometer that will stand the conditions. I remember that when we started using the Le Chatelier pyrometer, I gave a curve to the fireman to go by. I got some of the nicest curves you ever saw—so nice that the Art Department got jealous of the fireman, and we sent him to the Art Department.

The element of individuality comes into this strongly. We have had a good many systems of charts for kiln-burners. The fireman, when anything went wrong, could always explain that it was not his fault. I think that the charts increase the difficulty; it is hard to get a man to follow them. Then, too, there is a strong tendency for the man to pay more attention to the charts than to the kiln; and I have a great respect for a man with a shovel who pays strict attention to that. If he does not pay enough attention to the shovel, the results are bad.

Mr. Cannan: These charts do not distract the man's attention while firing. I think that a pyrometer is a good thing, if the fireman will use it; but it is of no good, if he will not. I believe we should pay as much attention to kiln work as to any other part of the business. It is a place where we put our money in; not to see it for three, four, or five days. We must have something that enables the fireman to protect himself from blame, and these charts and other such records protect the fireman. If he has a good distribution of heat, something else than the fireman must be wrong. If he has not these charts, they might say that the kiln was off-fired; and he could not protect himself. When he uses the chart, he will record the kiln when it is bad and when it is good. If he does this conscientiously, you will have very few troubles from kiln-firing.

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THE CALCULATION OF CERAMIC MIXTURES.

By HOMER F. STALEY, Columbus, O.

PURPOSE.

Modern science attempts to view data from every standpoint, arranging and rearranging experimental results and considering each arrangement in the light of known laws applicable to such an array. It then correlates the deductions obtained from the various methods of viewing the problem, and so finally, if the data is sufficiently ample and exact, lays down the laws governing the phenomena.

Inasmuch as it is the general, although happily not the universal, custom of ceramists to view their data on ceramic mixtures in only one arrangement, the empirical formula, it is the purpose of this paper to call to mind some other methods of attack. I shall confine myself more particularly to calculation of glaze and enamel mixtures, although the principles involved are for the most part applicable to body compositions. The methods I wish to discuss are:

I. Calculation from percentage amounts of raw materials.
II. Calculation from empirical formula.
III. Calculation from "Norms."
IV. Calculation from eutectics.
V. Calculation from empirical physical factors.

I. CALCULATION FROM PERCENTAGE AMOUNTS OF RAW MATERIALS.

This needs but passing notice. It is essentially the same as calculating on the basis of a raw batch of given weight. It, the simplest of all methods, has been used for hundreds of years by men who were able to get results; and is still used. When the number of ingredients is few, and the variations to be made in composition are small, this system works fairly well. When the reverse is true, and especially when the amount of volatile matter varies,

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the difficulties of drawing accurate conclusions as to the effect of variation in percentage amounts of raw batch become enormous. The mind of the man who attempts to work with complex batches is liable to become clogged with the mass of detail which he is called upon to remember.

This method has one great advantage over the succeeding one in that it deals with the minerals as actually used, and not with oxides, many of which have no real existence in the minerals from which they are supposed to be derived. This enables one to make allowance for the physical properties and conditions of the batch ingredients, a very important thing to do.

II. CALCULATION FROM EMPIRICAL FORMULA.

We object not to the use but to the abuse of the empirical formula.

Concerning this method, Seger says:[1] "It must, therefore, be stated in order to avoid errors of conception, that in this manner of expression, none of the different views of the constitutional groupings of the elements are antagonized in the least, and that the *formulae merely express that the elements indicated are present in certain proportions*, and it does this in a simple and graphic manner, from facts which can only be deduced from an analysis of the material."

Professor Orton,[2] referring to empirical formulae says: "These methods are merely mechanical aids to expression and are not in themselves a correct statement of chemical facts."

It is a decided disadvantage that the formulae are based on a recalculation of the gross analysis of the material, thus neglecting the mineralogical and physical condition in which the various elements are introduced. These neglected factors may be vastly more important when comparing two mixes than the formal similarity of ultimate analysis. This situation is of too common occurrence to need illustration or further comment.

[1] Collected Writings of Seger, Vol. II, page 562.

[2] Trans. Amer. Cer. Soc., Vol. III, page 80. See also Searle, Trans. Eng. Cer. Soc., Vol. VIII, page 40.

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If, to obviate this limitation, we try to work with empirical formulae, and at the same time keep in mind our batch, our problem becomes as complex as working with batch weights, thus annulling its one great advantage, *i. e.*, its graphic character. Used in this way, empirical formulae may be the means of hiding information rather than disseminating it. Addition of clay to a given glaze may be expressed in variation of the empirical formula of the glaze. It is much more simply expressed by variation of batch weights. Rather than discuss variation in properties as caused by variation in the ratio of RO to R_2O_3, total RO to SiO_2, and oxygen ratio, it would seem much more simple, and a great deal more accurate to discuss it for what it really is—addition of clay to a given glaze.

As ceramists, we are fundamentally interested in the physical properties of our glazes and but little interested in their chemical constitution. There are, however, grave objections to forgetting this limitation and reading a chemical significance into deductions made from the use of empirical formulae. The reasoning of the few who make this mistake seems to be of the sort which follows: "Increase of basic oxides causes crazing. This substance causes crazing. Therefore, this substance must be acting as a base in this mixture." Or,—"SiO_2 is an acid. Increase of SiO_2 stops crazing. Increase of this substance stops crazing. Therefore, this substance acts as an acid in this mixture." Such reasoning is unwarranted. It would put fluorine, one of the strongest of acids, in the basic class. SiO_2 stops crazing, not because it is an acid, but because of certain physical properties which SiO_2 and some of its salts possess. In the same way Fl causes crazing. Additions of MgO and ZnO, strong bases, have been used to stop crazing in glazes. Addition of MgO has long been a standard method of stopping crazing in enamels.

Any supposition that because glazes of a certain class conform roughly to a certain molecular ratio they must be alike chemically, seems to be another error of judgment. It can be shown by the application of experimental and

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mineralogical data that with a given SiO_2 content, change in the R.O. induces change in the kind and amount of minerals present in quite a kaleidoscopic manner. In fact, efforts to form such chemical likeness seem futile. We have little evidence to show that chemically similar substances have similar pyro-physical properties. Quite the contrary is evinced by the study of simple silicates, as for instance the orthosilicates of lead, sodium and calcium. *There seems but little foundation in fact for either of the conceptions that empirical formulae show chemical similarity of mixtures and that chemically similar mixtures should have like pyro-physical properties.*

Turning now to the points of advantage of calculation from empirical formula, we find only one, but that one is very weighty. *It presents its data in a simple and graphic manner.*

As a system of calculation it is easy to learn, and one that may be applied to a wide variety of mixtures. And since any system of arranging a great mass of data in a systematic manner is better than no system, the general use of empirical formulae has resulted in a marked advance in our empirical knowledge of the general relations between the ultimate analysis of ceramic batches and their pyro-physical properties. Since these relations are not at all definite and fixed, the knowledge gained can never be of more than a very general character, and the conclusions drawn must often be very hazy and even contradictory in nature.

Summary of Discussion on Calculation by Empirical Formulae.

I. It is a pseudo-chemical system, based upon the ultimate analysis of the batch to the neglect of important physical and mineralogical differences in the ingredients.

II. It has no innate chemical or physical significance.

III. It is graphic in character.

IV. Since the relationships it is capable of showing are not fixed or definite, the conclusions drawn from its use must be of an indefinite nature.

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III. CALCULATION FROM "NORMS."

This is an adaptation of the Quantitative Classification of the Igneous Rocks.[1] The basic idea of this classification is that the salts in solution in rock magmas may properly be considered to have the composition of those minerals which separate and crystallize when the magmas solidify. The "Norm" of a rock magma is its standard mineral constitution, as calculated by this method. It is granted that there is a possibility of ionization of these salts while in solution and also that, under some conditions, reactions may be set up in a given magma, such as to cause it to solidify into minerals other than those which they calculate should be formed. The fundamental conceptions underlying this method are, however, based upon several thousand analyses of igneous rocks and a thorough examination of a large quantity of mineralogical and experimental data.

There are only two conditions under which this method of calculation is of doubtful value: (1) When the magma contains large amounts of ferro-magnesian minerals; (2) or such gases, as water, hydrogen, or fluorine, under pressure. As neither of these conditions are met with in our work, this method of calculation should be especially accurate in determining the constitution of ceramic fusions.

The validity of the principles, upon which this system is based, is being tested out in an experimental way by various investigators, notably Day and his associates in the Geophysical Laboratory of the Carnegie Institute. It is worthy of note that, so far, no exceptions have been found to the principles laid down. As the systems studied in an experimental way grow more complex, the difficulties of technique and interpretation grow much greater. It is

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[1] "Quantitative Classification of Igneous Rocks," by Cross, Iddings, Pierson and Washington. University of Chicago Press.
"Journal of Geology," Vol. X, pp. 555–690.
"Igneous Rocks," Iddings, Vol. I, Wiley & Sons.
"Natural Classification of Igneous Rocks," Whitman Cross.
Quarterly Journal of the Geological Society, No. 263, Aug. 23, 1910.

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doubtful, therefore, if we will soon have a much more accurate statement of the minerals liable to separate from a given complex magma than the authors of this system of calculation have deduced from a study of thousands of actual crystallizations as evinced in the formation of igneous rocks.

The fundamental conclusions arrived at from the study of this great mass of data are:

I. The relative affinity of the common rock-forming oxides for SiO_2, beginning with the strongest, is: K_2O, Na_2O, CaO, MgO, FeO, Al_2O_3, Fe_2O_3.

II. The relative affinity of the oxides for Al_2O_3, beginning with the strongest, is the same: K_2O, Na_2O, CaO, MgO, FeO. Fe_2O_3 does not combine with Al_2O_3.

III. The molecular ratio of Al_2O_3 to other bases with which it enters into silicate combination is in many cases 1 : 1.[1]

IV. In case of low Al_2O_3 it may be replaced by Fe_2O_3.

V. Fe_2O_3, Al_2O_3 and SiO_2 are the only oxides of the above list that crystallize alone.

VI. Each base unites with the highest amount of Al_2O_3 and forms the highest silicate that it is capable of forming with the Al_2O_3 and SiO_2 available.

VII. The strength of the affinity for Al_2O_3 and SiO_2 of all the elements studied is proportionate to its position in the electromotive series.

From their position in the electromotive series and their general behavior in silicate magmas, we would not expect PbO and ZnO to form double silicates with Al_2O_3. In the presence of stronger bases and low silica we would expect PbO and ZnO to form orthosilicates; in fact we have evidence that PbO can exist as such in a silicate magma.[2]

The following salts, according to the above principles,

[1] This is quite generally true in the absence of gases under pressure, and of ferromagnesian minerals.

[2] Cooper, Shaw and Loomis, "Lead Silicates." American Chemical Journal, 1909, page 461.

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would be formed in a fusion which contained K_2O, Na_2O, CaO, PbO, ZnO, Al_2O_3 and SiO_2.

When SiO_2 is low, the following salts will be formed:

$K_2O,Al_2O_3,4SiO_2$	Leucite.
$Na_2O,Al_2O_3,2SiO_2$	Nephelite.
$CaO,Al_2O_3,2SiO_2$	Anorthite.
K_2O,SiO_2,	Potassium metasilicate.
Na_2O,SiO_2	Sodium metasilicate.
$CaO,{}^1/_2SiO_2$	Orthosilicate of calcium.
$ZnO,{}^1/_2SiO_2$	Orthosilicate of zinc.
$PbO,{}^1/_2SiO_2$	Orthosilicate of lead.

As SiO_2 increases, the above compounds are converted to higher silicates as follows:

CaO $\frac{1}{2}SiO_2$, ZnO $\frac{1}{2}SiO_2$, PbO $\frac{1}{2}SiO_2$ to
CaO SiO_2, ZnO SiO_2,[1] PBO SiO_2 respectively.
K_2O, Al_2O_3, $4SiO_2$ to K_2O, Al_2O_3, $6SiO_2$ Orthoclase.
Na_2O, Al_2O_3, $2SiO_2$ to Na_2O, Al_2O_3, $6SiO_2$ Albite.
Al_2O_3, SiO_2, Sillimanite, depending upon conditions, may or may not be formed.

Remarks on Formation of Norms.—(1) The conditions permitting the formation of sillimanite are well defined.

(*a*) This mineral is not necessarily found when free Al_2O_3 and SiO_2 occur together.

(*b*) If there is an excess of both Al_2O_3 and SiO_2, after the formation of the higher silicate group, sillimanite may be formed.

This makes plain why Vernansky was not able to produce sillimanite from fusions of feldspar with SiO_2.

(*c*) Introduction of PbO into a magma would not effect the excess of Al_2O_3 capable of entering sillimanite, and would reduce excess SiO_2 but slightly. At the same time it would make the magma more fluid, thus affording a better medium for crystallization. This throws light on Mellor's statement that sillimanite can be produced at a lower temperature in the presence of PbO and that the lead oxide seems to have a catalytic action. It seems

[1] Sufficient data are not at hand to determine definitely whether zinc and lead orthosilicates pass over to metasilicates before or after the feldspathoids form feldspar.

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probable that most so-called catalytic actions in silicate fusions consist in producing a better medium for the consummation of reaction.

(2) Devitrification in high silica glass is decreased by adding Al_2O_3. The norm of ordinary lime silica glass is:

$$0.50\ Na_2O \quad 0.50\ SiO_2$$
$$0.50\ CaO \quad 0.50\ SiO_2$$
$$1.50\ SiO_2 \quad \text{uncombined.}$$

Now if 0.05 Al_2O_3 is added, the norm becomes:

$$0.05\ Na_2O \quad 0.05\ Al_2O_3, \quad 0.30\ SiO_2 \quad \text{Albite.}$$
$$0.45\ Na_2O \quad 0.45\ SiO_2$$
$$0.50\ CaO \quad 0.50\ SiO_2$$
$$1.25\ SiO_2 \text{ uncombined.}$$

Thus by the addition of only 0.05 Al_2O_3, uncombined SiO_2 has been reduced by 0.25.

(3) On the other hand devitrification in basic glasses is decreased by adding SiO_2. (See "Crystalline Glazes," by Purdy and Krehbiel, *Trans. A. C. S.*, Vol. IX, p. 402.)

Glass No. 1, which was completely devitrified, has a norm as follows:

$$0.5\ Na_2O \quad 0.5\ SiO_2$$
$$0.5\ CaO \quad 0.5\ SiO_2$$

corresponding to high concentration of the easily crystallizable substance, $CaO\ SiO_2$.

Glass No. 2, with the following norm,

$$0.5\ Na_2O \quad 0.5\ SiO_2$$
$$0.5\ CaO \quad 0.5\ SiO_2$$
$$0.5\ SiO_2 \text{ uncombined,}$$

corresponding to less concentration of $CaO\ SiO_2$, was less devitrified. Devitrification decreased in the other members of the series as the concentration of $CaO\ SiO_2$ decreased.

In the same article, Messrs. Purdy and Krehbiel have shown that as the concentration of $ZnO\ SiO_2$, an easily crystallizable substance, decreased, crystallization decreased.

Glaze No. 384, p. 378, with the following norm,

$$\left.\begin{array}{ll} 0.3\ Na_2O & 0.3\ SiO_2 \\ 0.7\ ZnO & 0.7\ SiO_2 \\ 0.5\ SiO_2 \text{ uncombined} & \end{array}\right\} \text{Molecular concentration of } ZnO\ SiO_2 \text{ 7 in a total of 15,}$$

had many small crystals.

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Glaze No. 394, p. 379, having the following norm,

$$\left.\begin{array}{ll} 0.3\ Na_2O & 0.3\ SiO_2 \\ 0.7\ ZnO & 0.7\ SiO_2 \\ 0.6\ SiO_2 \text{ uncombined} & \end{array}\right\} \begin{array}{l}\text{Molecular concentration of ZnO } SiO_2 \\ 7 \text{ in a total of } 16,\end{array}$$

had a few small crystals. If it is held that ZnO 1/2 SiO_2 is the crystalline substance, the principle of decrease of crystallization with molecular concentration would still hold.

4. The increase of fusibility due to additions of small amounts of clay to high lime mixtures low in Al_2O_3 can readily be explained by the fact that the simple calcium silicates, materials of high concentration in the magma, are converted into anorthite, which is of low concentration. Eutectic proportions would thus be more nearly approached, and the lime compounds would all be fluid after melting.

5. Enough has been said to show that according to norms, the amount of free SiO_2 and the kind of silicate salts found in a mixture does not depend upon the oxygen ratio, but on the total SiO_2 and the kind of bases forming the RO.

The following two mixtures have the same oxygen ratio:

I		II		
$0.5\ Na_2O$ $0.5\ CaO$ }	$1.5\ SiO_2$.	$0.5\ Na_2O$ $0.5\ CaO$ }	$0.20\ Al_2O_3$,	$2.4\ SiO_2$
O. R. 1 : 3		O. R. 1 : 3		

Norm.		Norm.		
$0.5\ Na_2O$	$0.5\ SiO_2$	$0.2\ Na_2O$	$0.20\ Al_2O_3$	$1.20\ SiO_2$
$0.5\ CaO$	$0.5\ SiO_2$	$0.3\ Na_2O$		$0.3\ SiO_2$
	$0.5\ SiO_2$	$0.5\ CaO$		$0.5\ SiO_2$
				$0.4\ SiO_2$

According to ceramic usage, both the above formulae would be polysilicates. By calculation of norms, I is a mixture of metasilicates with free SiO_2, while II is shown as a mixture of metasilicates with a polysilicate and less free SiO_2.

Of course, in applying to glazes any such reasoning as is involved in the use of norms, the probability of the

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glaze taking up material from the body must be taken into consideration. However, it does not seem that it would be an important factor in such work as crystalline glazes. In the first place, it must be remembered that a substance will not be taken into solution unless it is present in the solution in less than eutectic proportions, or unless it is needed to fill the requirements of some unsatisfied chemical valence. The only minerals that could be taken up from an ordinary body would be clay, flint, and feldspar, and these would make the layer of glaze next to the body so viscous that the absorbed material would not be diffused through the rest of the glaze, and since crystalline glazes are thick, the bulk of the glaze would not be affected.

Conclusions on Method of Calculation by Norms.— The use of norms is restricted to a narrow field and must at all times be more or less hypothetical, but it gives a more rational means of attacking some problems than can be obtained in any other way.

IV. CALCULATION FROM EUTECTICS.

Quite a number of eutectics between pairs of ceramic materials have been located, and considerable work has been done toward the location of several ternary or three-component eutectics.[1] We have all watched the accumulation of such data with interest. We logically assume that if we are able to locate the eutectics in our mixtures, we will be in a position to understand their pyro-physical properties much better. In the course of time we would be able to classify any given composition according to its relation to some eutectic mixture. Such a system would be calculation from eutectics.

In another place we have discussed the bearing the formation of melting point and deformation eutectics have on the pyro-physical properties of ceramic mixtures. It will be sufficient to state here that while the study of silicate mixtures from the standpoint of physical chemistry

[1] Jour. of Ind. and Eng. Chem., Vol. 3, No. 4, April, 1911.

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is interesting and instructive yet, owing to the lack of experimental data, no system of calculation can be built up on it that as yet will take the place of empirical systems.

V. CALCULATION FROM EMPIRICAL PHYSICAL FACTORS.

From a study of the foregoing systems of calculation, we gather that any system of calculation of glazes and enamels of general utility must have the following characteristics:

I. *It must not be affected by the amount of volatile matter in the raw batch.* The presence of large and varying amounts of volatile matter is the cause of confusion in calculating from batch weights.

II. *It must take into consideration the physical and mineralogical condition of the ingredients.* Failure to do this is the great limitation of the empirical formulae system.

III. *It must be capable of indicating primarily the pyro-physical properties of the mixture.* The physical properties of a mixture as developed by heat treatment are what determine their value for ceramic purposes. It will be an incidental advantage if the system renders easy a calculation of the final mineralogical constitution, as this has a bearing on the ultimate viscosity of the mixture, and also on the phenomenon of crystallization.

IV. *It must be graphic in character.* This is the one great advantage of calculation by empirical formulae.

The system which we wish to suggest is capable of meeting all these requirements and is, we believe, a happy combination of the best in each of the other systems discussed. It consists essentially of the following procedure *in any one class of glazes or enamels*:

1. Calculation of the melted weight of the minerals composing the batch. This is readily done by the use of factors. For purposes of calculation the conventional assumption as to percentage of volatile ingredients are sufficient.

2. Experimental determination of the relative pyro-physical effect of the various melted minerals pound for

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pound. It is also necessary to determine the pyro-physical effect, if any, of a change in the physical condition of each mineral. From these determinations, such factor numbers or coefficients can be assigned to the various melted minerals in various physical conditions as express their relative pyro-physical effect.

3. Combination of the melted minerals of like pyro-physical effect into groups, and arrangement of the groups in such manner as best expresses their pyro-physical relations. Then by arranging any glaze of this type in this form, multiplying by the proper pyro-physical factors and adding the products in each group, two or three numbers can be obtained whose ratio expresses in a very graphic manner the pyro-physical properties of the mixture.

It will be noticed that calculation in pounds of melted weight is advocated rather than in so-called molecules or chemical equivalents. This is done for two reasons. First, it is easier, and second, it is believed to be more scientific. We have no means of knowing the true molecular weights of the substances we use, and much less means of knowing the molecular weight of the compounds found in our igneous fusions. The molecular weights given in text books are simply conventional. The true molecular weight may be several times these. We know that outside of the R O. oxides, the so-called chemical equivalents are not chemically equivalent, one "equivalent" of Al_2O_3 being chemically equal to 3 R O., while 1 R O. is equivalent, chemically, to 1/2 to 1-1/2 SiO_2 and 1/3 to 2 B_2O_3, according to circumstances. The conventional equivalents used by ceramists are, as we all know, simply the arithmetical units adopted by metallurgists for convenience in calculation and have no true chemical or physical meaning. When we remember the slight connection so far proven, between true chemical constitution and physical properties, to try to correlate the pyro-physical properties of our glasses with these arbitrary units seems rather futile. Moreover, the laws of physics to which we must look more and more for interpretation of the peculiarities of the physical properties of

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our products are based upon percentage composition, and cannot be applied to "equivalent weights."

In order that our results may be checked by others, it is important that in determining relative pyro-physical effects, we use as a basis of comparison substances which can be duplicated. For instance, in enamels practically all the R O. oxides are used as fluxes, while sand, flint and various feldspars are used as refractories. Now red lead and standard dry-ground flint are materials that can be duplicated anywhere in America, so by making 1 pound of PbO from red lead and 1 pound standard ground flint, the standards for fluxing power and refractoriness respectively, we get results that can be duplicated by others.

Of course it is not necessary to reduce the melted weight to a percentage basis, although this is convenient in some cases. Some group may be taken as one hundred or one, just as in empirical formulae.

In Coe's work on "Ground Coat Enamels," this volume, he kept the easily fusible constituents constant, and added such amounts of the various refractory materials as would give him like fusibility. In my own work in enamels (see "Control of Fusibility in Enamels," this volume), I find it convenient to reduce the melted weight to percentages as this gives me several important ratios direct.

As to the labor involved in working out such a scheme, it need not be great for any one class of glazes.

I developed such a system for cast iron enamels, working on it at odd times for two years. The number of materials covered was over twenty and the amount of labor involved was consequently greater than any one man would be called upon to do with glazes.

The results obtained have amply repaid the effort. I have used this system[1] in three different factories, with three different sets of chemicals, including six different feldspars. It has given consistent and satisfactory results under all conditions.

[1] This plan is of the same sort as the one used by Burt and described under the title "Coefficient Equivalents" in Vol. VI, Trans. Amer. Cer. Soc.

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It might be urged against such a system that it is not general enough, that it would make a special case of every class of glazes, and every clay or feldspar used in a given class. This would be true only because every class of glazes *is* a special case in which the vital relations between the minerals used are different from the other classes. Moreover, there are clays and clays, and the same way with feldspars. If they have different pyro-physical effects, this must necessarily be allowed for.

FINAL SUMMARY.

I. Calculation from percentages or batch weights can be used with advantage only in very simple mixtures.

II. Calculation from empirical formulae is not adapted to giving definite results. The method can lay no claim to a scientific foundation.

III. Calculation from norms can be used only in very special cases.

IV. Calculation from eutectics is not practicable in our present state of knowledge.

V. Calculation from empirical physical factors determined separately for each class of ceramic mixtures is suggested as being a method capable of giving the exact control of mixtures necessary in actual factory practice.

DISCUSSION.

Mr. Binns: If this method had been introduced at the time when the molecular formula, or the empirical formula was, there might not have been any use for the latter. So many of us have now got into the habit of thinking in terms of the empirical formula, and it has been so satisfactory, that there must be good reason for making a change before we do so.

Mr. Staley: In a paper on enamels, I figure the system out step by step for twelve different formulae, from one recipe to another, keeping the values the same, and showing how I derive my pyro-physical factors. I did not figure out

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my empirical formula until I was on the train, on the road to Trenton, and the papers were all typewritten. I then found that by my method they have exactly the same pyro-physical ratio (that is, 2.13 : 1) while by the empirical formula, one has an oxygen ratio of 1 : 0.94 while the other has an oxygen ratio of 1 : 1.43.

Mr. Stover: It makes a good deal of difference, when figuring for flint, whether you are figuring for body or for glaze.

Mr. Staley: Even in enamels, it makes a great deal of difference.

Mr. Binns: He says that the difference between coarse-ground flint and fine-ground flint is vital, and a few moments ago he said that it was standard. What becomes of the standard, if there is a difference between coarse and fine-ground flint?

Mr. Staley: What I meant was the difference between sand and ground flint. I have bought flint from a dozen factories, and could see no material difference among them; but there was a difference between dry-ground flint and glass sand such as a great many of the enamel plants use. If we use dry-ground flint in America, and some man, who is employed where they have the wet ground, should try to use the same factors, he would get into trouble. Every man must make a special case of his special material. You cannot get any one system to annihilate space and destroy the physical properties and differences in our material.

NOTES SUBMITTED AFTER HAVING READ THE PAPER.

Prof. Binns: I find a difficulty in discussing this paper because Mr. Staley has not given any idea as to the working of his proposed method of calculation. He speaks of a pound of lead oxide as a unit but gives no explanation of the way in which other substances can be referred to this. He objects to the complication of the formula but seems to offer an alternative which is even more involved. I fully admit the propriety of considering the natural con-

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dition of the materials employed but this must be a matter of experience in either case. I have never considered that the formula affords a royal road to the understanding of ceramic mixtures but it is now so well established and so universally understood that any suggested substitute must be of well recognized superiority and of unimpeachable value.

Mr. Kerr: In the consideration of any problem it is always of great assistance to have clearly outlined the several methods by which the problem may be attacked, and in the field of ceramic calculation it is a step in the right direction that such a presentation of methods has been made.

In considering this paper let us start with the assumption that the empirical formula is not by any means perfect, and that improvements in methods of expressing and calculating ceramic mixtures are greatly needed; in that, all ceramists are agreed. Let us also bear in mind that our knowledge of silicate chemistry, and especially our knowledge of the physical side of silicate chemistry, is very limited indeed. Some of the systems comprising SiO_2 and one other component have been carefully studied, but beyond that, our knowledge extends only a very little way. Bearing in mind both the need of improvements in methods of calculation and the limitations of our knowledge of silicate chemistry, let us consider the points raised in the paper under discussion.

In referring to "Calculation from Empirical Formulae," the author states that "we are fundamentally interested in the physical properties of our glazes and but little interested in their chemical constitution." In a very narrow and restricted sense that is a true statement of the case. But in the broad scientific sense we are intensely interested in the chemical constitution of our ceramic materials because experience in other chemical fields has shown us conclusively that it is only upon well-grounded knowledge of chemical constitution and the relation of chemical constitution to physical properties under various conditions that scientific progress can be made. Let us not forget that chemical con-

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stitution, especially as affected by physical conditions, is the vital thing underlying all ceramic science. It is not the physical condition that is the important part of the law; it is the chemical constitution as affected by the physical condition.

Concerning the incorrect reasoning to which the author refers in considering the empirical formula, neither of the illustrations given offers any argument whatever against the empirical formula. Both cases cited are cases of incorrectly constructed argument, and the conclusions drawn are, therefore, void. Take the second case. The major premise is "Increase of SiO_2 stops crazing" and not that "SiO_2 is an acid." Even then the argument cannot ho d for the major premise does not limit the number of, or variations in the materials which do stop crazing. Study of all such arguments shows that the trouble is not with the empirical formula, but either with our arguments themselves or the definitions involved in the arguments.

The author sums up the case against the empirical formula under four heads:

1. "It is a pseudo-chemical system and based upon the ultimate analysis of the batch to the neglect of important physical and mineralogical differences in the ingredients." The criticism is well taken.

2. "It has no innate chemical or physical significance." So far as this is true, it is because our knowledge of the physical chemistry of the silicates is too limited to supply the needed significance. By *any* method of calculation the effect of variations in treatment under different conditions must be taken into account.

3. "It is graphic in character." The author has clearly pointed out the great advantage of graphic representation.

4. "Since the relationships it is capable of showing are not fixed or definite, the conclusions drawn from its use must be of an indefinite nature." At present this objection holds to some extent, but if our knowledge were extended (as it certainly will be) so that we could give

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definite meaning to the various relationships under any given conditions, then our conclusions could be equally definite.

In discussing "Calculation from Norms," the author has very properly called special attention to the work done by Cross, Iddings, Piersson, Washington and others in the field of igneous rocks. This work is of the greatest importance to ceramists and it should be very carefully followed by all. But it must be borne in mind that the work deals with igneous rocks and not with ceramic bodies. These eminent petrologists do not claim that in the laboratory or in the manufacturing plant the conditions obtaining in the making of igneous rocks will be duplicated. There is a vast difference between the physical conditions operating in the two cases. Our most eminent physical chemists have made but little progress in the study of three-component systems, and when one considers that in ceramic mixtures the number of components is never as low as three, the necessity of great care in drawing conclusions based upon the laws of physical chemistry as they are known to-day becomes very evident.

The work done upon igneous rocks represents a wonderful stride in the field of silicate chemistry, but there is at present no justification for assuming that the correlations of fact thus obtained may be taken as laws operating in the field of ceramic mixtures where the physical conditions are so widely different. It has never been proven that these various naturally occurring silicates are actually formed in ceramic mixtures. Certainly the conditions governing the formation of sillimanite *in ceramic mixtures* are not as simple as those given.

In further discussion of "Calculation from Norms," the author gives formulae for two mixtures having oxygen ratio 1 : 3, and states that "I is a mixture of metasilicates with free SiO_2, while II is a mixture of metasilicates with a polysilicate and free SiO_2." No proof has yet been offered that these statements are true. Certainly they would not be true under *all* conditions. Our present knowledge of

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the physical chemistry of these silicates does not seem to warrant statements beyond the expression of the empirical formula.

The subject of eutectics is a most interesting and most instructive one, and a continued study of the problems is certain to bring to light a wealth of most important information. As the author has pointed out, the data now at hand are not sufficient to make possible the drawing of general conclusions.

Under "Calculation from Empirical Physical Factors," the author says that the method "consists essentially of the following procedure, in any one class of glazes or enamels:

1. "Calculation of the melted weights of the minerals composing the batch....."

2. "Experimental determination of the relative pyro-physical effect of the various melted minerals pound for pound"—also the effect of any "change in the physical condition of each mineral."

3. "Combination of the melted minerals of like pyro-physical effect into groups—."

In the calculation of melted weights (point 1) it must be remembered that with certain ceramic materials the conditions under which melting occurs alter both the weight of the melted material and its composition. How can a melted weight be stated, therefore, unless the accompanying conditions are specified?

Concerning point 2, the pyro-physical effect of the melted minerals will be influenced by (1) variations in the physical condition of the material itself, as the author has pointed out, (2) variations in the character of the mix in which used, and (3) variations in the conditions of use, especially as to time, temperature, etc.

It does not seem possible at the present time to arrange a grouping of melted minerals (point 3) that will hold under even small variations of conditions.

From a consideration of the essential points in the procedure it is very hard to see that the proposed method is based in any way upon scientific knowledge. The empir-

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ical formulae system with all its acknowledged faults is to some extent a scientific tool, and with every increase in our knowledge of ceramic chemistry there will come a corresponding increase in the meaning and value of the empirical formula.

It is true that in certain ceramic materials, equivalents are not strictly scientific figures, but they are based upon molecular weights which are strictly scientific, and any errors which exist are errors of deducing chemical equivalents and not errors in the molecular weights. Such errors will in time be corrected. One cannot agree with the author that molecular weights are meaningless conventional figures.

"By making 1 pound of PbO from red lead and 1 pound of standard ground flint, the standards for fluxing power and refractoriness respectively, we get results that can be duplicated by others." It is hard to see how such standards can be of any value from the standpoint of the future development of ceramic science. Even omitting the most important consideration that we are building foundations for future development, these standards are open to several vital criticisms. They will be affected by variations in (1) purity, (2) temperature, (3) time of fusing, (4) furnace conditions, etc., to such an extent that results cannot be duplicated closely enough to warrant the drawing of conclusions from tests made. Further it is not possible to draw a sharp line of distinction between fluxes and refractories.

The contention is made that "every class of glazes is a special case," and that consequently each class must be dealt with separately. Undoubtedly each class is a special case but it is a special case only because of the preponderance of the effect of certain conditions. The general laws governing these conditions must be sought out and ceramic knowledge must be extended until it becomes clear that *the same general laws cover the entire field*, and that the understanding of the special cases demands adaptation of

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the general laws and not the formulation of specific laws for specific cases.

Further, physical conditions must be taken into account throughout a process. The physical condition of the raw materials is of great importance, as the author has shown. But of equal or greater importance are the physical conditions under which the materials react during the manufacturing process. This latter point should always be borne in mind, but unfortunately it is frequently overlooked.

Mr. Potts: There is in *Sprechsaal* for May 11, 1911, (Vol. 44, No. 19, p. 278) an article entitled "The Influence of Metallic Oxides upon Lead Glazes" by Fritz Kraze and Alex Popoff, which has considerable bearing upon the "Calculation from Empirical Physical Factors," which Professor Staley advocates.

These investigators used a glaze of the formula

$$1\ RO,\quad 0.084\ Al_2O_3,\quad 0.969\ SiO_2.$$

The R O. was made up as follows: Each glaze of the series contained 0.8 PbO and 0.2 of one of the following oxides: K_2O, Na_2O, CaO, MgO, BaO, SrO, ZnO, MnO, Fe_2O_3, Cr_2O_3, Co_2O_3, Ni_2O_3 and CuO, making thirteen glazes in the series, each glaze differing from the rest only in the metallic oxide contained. They sought information as to the effect of these oxides on the crazing and fusibility of lead glazes.

The relative fusibility was obtained as follows: Each raw glaze was moulded into a cone and these cones were attached to a biscuit plate. The plate bearing the cones was then set at an angle a little less than 45° in a muffle kiln and burned until the tip of the most refractory cone just touched the plate. The distance which each glaze flowed under this heat treatment was measured and taken as an index of the fluxing action of the metallic oxide contained.

Accompanying the article is a chart which shows graphically the results obtained. From this chart the following data have been taken or calculated.

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Metallic oxide.	Taken. Equivalent weight.	Distance glaze flowed in 50th's of an inch measured on the chart.	Calculated. Ratio of equivalent weights MgO, taken as unity.	Relative fluxing action MgO = 1
MgO.....	40.0	27	1.0	1.0
CaO.....	56.0	41	1.4	1.5
Na_2O.....	62.0	45	1.55	1.66
K_2O.....	96.2	55	2.355	2.03
SrO.....	103.62	95	2.59	3.4
BaO[1].....	153.4	63	3.835	2.32

It is from data like this that Professor Staley would calculate his empirical physical factors. In this particular glaze and with this particular substitution the fusibility of the several glazes is roughly proportional to the equivalent weight of the oxide used. However, we have every assurance that these factors would not be applicable to more complex glazes and indeed with our present knowledge, I doubt very much that any advantage commensurate with the labor involved would be gained by determining such factors for every special type of glaze.

NOTES PREPARED AFTER READING MR. KERR'S DISCUSSION.

Mr. Staley: I have read Mr. Kerr's discussion with a great deal of interest but I can hardly agree with some of his ideas. In fact, the errors of conception displayed in this discussion show how necessary it is that some of the points mentioned in my paper be strongly emphasized.

Much depends upon our conception of what purpose a system of ceramic calculation is intended to serve. I advanced my system of ceramic calculation for use in the actual manufacture of ceramic wares.

Mr. Kerr is not in full accord with my statement that "as ceramists we are fundamentally interested in the physical properties of our glazes and but little interested

[1] BaO was introduced as carbonate; it is well known that the oxide is a much more active agent than the carbonate.

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in their chemical constitution." If our manufacturers are trying to produce ware covered with glazes which they can guarantee to be a mixture of metasilicates, orthosilicates and polysilicates in certain definite proportions, then they are fundamentally interested in the chemical constitution of their glazes. If they are trying to produce ware covered with fine glossy glazes which they can guarantee not to craze or shiver, and to be free from pin holes, then they are fundamentally interested in the physical properties of their wares. If we knew enough about the chemical constitution of our glazes to believe that similarity of chemical constitution would mean like pyro-physical properties, there would be good reasons for making a study of chemical constitution of glazes. But such studies must be conducted in our universities rather than in our factories.

In my paper I quoted a couple of cases of incorrect reasoning supposed to be based on the use of empirical formulae. Mr. Kerr explains at some length that he sees the point.

When he comes to my summary of the discussion on calculation by Empirical Formulae, Mr. Kerr speaks of it as a summary of "the case against the empirical formula." This is a mistake. I was not attacking the empirical formula and stated explicitly that I objected "not to the use but the abuse of the empirical formula." Howbeit, we find that he agrees without question with two of my conclusions. He admits that the other two are true in part at least, but claims they will not hold when our knowledge of the physical chemistry of the silicates is vastly extended "so that we could give definite meaning to the various relationships under any given condition." When this happy time comes, if ever, we know from our knowledge of the methods used in physical chemistry that from the very complexity of the problems involved, as emphasized by Mr. Kerr, the physical chemists will have to use a great deal more complicated and a great deal more exact representation of the constitution of our magmas and the physical factors involved, than that given by the empirical

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formula. In the meantime we must manufacture, every year, in this country alone some $250,000,000 worth of claywares, enameled wares and glass. If the fourth point of my summary holds true, it alone would be a grave objection to the use of the empirical formula.

Mr. Kerr's statement of the care to be taken in the application of the use of norms to ceramic mixtures is hardly more explicit than my own. The whole discussion of norms was given simply for its suggestiveness. When discussing calculation by empirical formulae, Mr. Kerr urges us to study the relations between the chemical constitution of our magmas and their physical properties and also to use empirical formulae because our knowledge of physical chemistry is going to tell us what the formulae mean. When discussing the use of norms simply as a possible indication of the minerals that will crystallize out of a magma, he tells us that our mixtures are so complicated that we know little about the constituents present and must "use great care in drawing conclusions based on the laws of physical chemistry as they are known to-day."

The use of norms was suggested as a practical hint, not as a scientific certainty. The fact is, however, that when working in silicate magmas, physical chemists of good repute use methods similar to those involved in calculation by norms in order to have some indication as where to look for crystallization of new compounds.[1] I do not believe that any physical chemist would attempt to use such a hybrid thing as the empirical formula as a scientific tool.

When discussing calculation from empirical factors, Mr. Kerr takes several exceptions to the method proposed. He inquires: How can a melted weight be stated, therefore, unless the accompanying conditions are specified? In reply, I would state that "the accompanying conditions are specified" by the statement that the procedure is to be applied, and the results obtained are to be used only "in

[1] Day and Shepherd, "Lime Silica Series of Minerals," Am. Jour. Sci., 4th Series, XXII, p. 267.

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any one class of glazes or enamels." In passing, I might call attention to the fact that the empirical formula which he defends so valiantly is based on calculated melted weights.

He states that the pyro-physical effect of the melted minerals will be influenced by (1) variations in the physical condition of the material itself; (2) variation in the character of the mix in which used; and (3) variations in the conditions of the use especially as to time, temperature, etc. Exactly, in fact, these three statements are a more forceful array of arguments in favor of my system than I myself have ever been able to formulate. I avoid "variation in the character of the mix in which used and variations in the conditions of use, especially as to time, temperature, etc.," by confining the procedure and the results obtained to one class of glazes or enamels. I would determine experimentally "the effect of variations in the physical conditions of the material itself." It is hard for me to see how any man can make these statements and then reject the use of a system built on these arguments and urge the use of the empirical formula system which does not meet them.

In discussing the use of the PbO from red lead and standard ground flint as standards for fluxing power and refractoriness respectively, Mr. Kerr makes a strong argument for my proposal to make a special case of each class of glaze or enamel. Incidentally he misquotes me. I proposed these materials as standards in enamels only, and not in all classes of ceramic mixtures. He says these standards will be effected by (1) purity, (2) temperature, (3) time of fusing, (4) furnace conditions, etc., to such an extent that results cannot be duplicated closely enough to warrant the drawing of conclusions from tests made. As to purity, I can only say after having used many carloads of these materials, including most of the brands on the American market, I have never known the small amount of impurities, that may sometimes have been present, to have any noticeable effect on their action in glasses rich in fluxing materials

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like glazes and enamels. The possibility that these two materials might not serve as standards for fluxing power and refractoriness in some other class of ceramic products emphasizes the fact that each class should be treated as a special case. Variations in the second, third, and fourth points he mentions would certainly be reduced to a minimum if comparisons were made in only one class of material manufactured in one general way. Contrary to his opinion that results can not be duplicated close enough to warrant drawing conclusions, we have the fact that when much fewer precautions than indicated here have been taken to secure duplication of conditions, results have been duplicated in ceramic work time and again. If this were not possible, what would be the use of publishing recipes in the shape of empirical formulae with their attendant uncertainty as to batch composition and the physical condition of the same, or in fact, what would be the use of keeping any record of our results at all?

We now came to a point on which I must fairly take issue with Mr. Kerr. He states that ceramic equivalents are "based on molecular weights which are strictly scientific." This is not a question of opinion, but of fact, and so is capable of being referred to authorities. I presume that Mr. Kerr will grant that we use our materials in the solid state or in igneous fusions. Nernst says:[1] "There is no method known at the present time which leads to a knowledge of the molecular weight of solids; indeed our molecular conceptions of the nature of the solid state are very vague." Morga nsays:[2] "We cannot define molecular weight in the solid state." Ostwald says:[3] "The molar concept has so far obtained no importance among solids." Similar statements can be found in any first-class physical chemistry.

In regard to our knowledge of molecular weights in igneous fusions, I quote Shepherd, Rankin and Wright as

[1] Theoretical Chemistry, Fourth Edition, page 272.
[2] Elements of Physical Chemistry, page 102.
[3] Fundamental Principles of Chemistry, page 288.

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follows:[1] "It is of course desirable to know the molecular weight of the various minerals, whether or not they dissociate in solution, and the effect of these phenomena on their interreactions. At the present time such questions are practically unanswerable. The molecular weight of salts in aqueous solution is determined by the lowering of the freezing point, but even at this low temperature and with the most delicate apparatus, an error of five per cent. is regarded as doing very well. Not only must the temperatures be measured to the nearest hundredth of a degree, but the formulae have thus far been found to apply only to infinitely dilute solutions—never over one per cent. Silicate melts are too viscous to be stirred, and freezing occurs in a region of variable temperature distribution and always over an interval of a whole degree or more. Furthermore, we have as yet no means of knowing that the *fundamental assumptions* underlying the van't Hoff-Raoult relation hold true for silicates. We ought, therefore, to hesitate before forcing the results thus far obtained into formulae which were deduced for wholly different conditions and which apply none too accurately even then. Obviously, the calculation of molecular weights from concentrations of ten, twenty, and even fifty per cent., as has sometimes been done, can serve no useful purpose.

"A glance at the technique of measurement of conductivity in aqueous solutions will reveal how unwise are generalizations based on experiments with the conductivity of silicates. Maintaining a constant temperature throughout even a relatively small volume is extremely difficult at a temperature of 1200° C. Electrodes and containing vessels can not be maintained constant in shape or dimensions, nor can perfect or constant contact relations between the electrodes and the melt be assumed. Until such essential conditions can be supplied, we cannot hope to derive much useful data from merely passing the electric current through

[1] The Binary System of Alumina with Silica, Lime and Magnesia. Amer. Jour. Sci., 4th Series, XXXII, p. 294.

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a silicate. The effect of high and varying viscosity on conductivity is unknown."

Mr. Kerr has an exalted opinion of the scientific value of the empirical formula. I am afraid this appreciation cannot be shared by those who are familiar with the assumptions on which it is founded[1] or by those who have any appreciation of modern silicate chemistry.[2]

The empirical formula may be convenient but it is certainly not scientific. I believe the quotations from Seger and Professor Orton, given in the first part of my article, define definitely the status of the empirical formula.

In regard to building a foundation for future ceramic science and to the necessity for searching out the general law and applying it to the special case, I wish to say that he would have us work the modern scientific method backward. If we ever want to have a scientific understanding of the relations between composition and physical properties of ceramic mixtures, we must shelf some of our hastily conceived generalizations and collect a body of actual experimental data. We will then be in a position to make provisional generalizations—if there are generalizations to be made.

The experimental determination of the relative amounts of the various materials of various physical condition necessary to produce a given pyro-physical effect in different classes of ceramic mixtures would be a rough flaying of the way for a scientific understanding of some of our ceramic problems.

NOTE PREPARED AFTER READING MR. STALEY'S DISCUSSION.

Mr. Kerr: I hope that the spirit of personal abuse will not gain ground in the Transactions of the Society.

There are three points in further discussion to which I wish to direct brief attention.

[1] Classification and Nomenclature of the Silicates, by Professor Orton, Vol. III, Trans. Amer. Cer. Soc.

[2] Iddings, "Igneous Rocks," Chapter IV.

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1. Are manufacturers of ceramic wares interested in the chemical constitution of their products?

2. What connection have molecular weights with chemical science?

3. Is it working backward to develop laws in the laboratory and then study their application in commercial work?

In answer to the first question we can point to the iron and steel industry. Probably the directors of some of our large iron and steel plants are not familiar with the iron-carbon diagram, and it is easily conceivable that many of the stockholders have never heard of ferrite but it is universally conceded that were it not for the development in the laboratory of the study of the chemical constitution of the iron compounds and alloys, the present position of iron and steel manufacture would not have been possible. Probably the ceramic manufacturer will never be interested directly in the chemical constitution of his wares, but there is a greatly increasing number of people who believe that study of the constitution of the silicates and the laws governing their formation and properties is the path along which permanent and safe development must come.

As to molecular weights, it must be remembered that as they are at present used in the general field of chemistry, they are simply convenient means of expressing combinations of atomic weights, and in that sense, the one in which they are generally understood, their intimate connection with the development of chemical science needs no proof. Whether or not the true molecular weight is a multiple of the combination of atomic weights used, does not affect the reasoning involved.

The answer to the third point is self-evident. The fundamental idea of laboratory investigation is to make possible the study of any problem under conditions where all the factors are capable of being regulated. Thus, one point may be studied at a time. Laws or theories may be evolved in this way, and by a laboratory study of the effects of the various governing conditions, the laws

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may be applied to commercial work. Of what use are laws if we must wait until the maximum perfection (or even partial perfection) in commercial work has served to bring them out? Laws lead to a development and not development to laws. Surely the logical method is to study in the laboratory, laws and conditions governing them and then to apply those laws under the conditions of manufacture.

Silicate chemistry is exceedingly difficult as all chemists know, and comparatively little progress has as yet been made, but it is not safe to understand this to mean that very little progress will ever be made. If it is possible, all courses should be avoided that lead to a splitting up of the silicate field into disconnected parts each of which has its own peculiar language unintelligible to the rest.

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NOTE ON THE MANUFACTURE OF SILICA BRICK BY THE "ANACONDA" METHOD.

By A. F. GREAVES-WALKER.

The method of manufacturing silica brick described in this note was undoubtedly originated by the Amalgamated Copper Co., of Anaconda, Montana. So far as can be learned, it is now being used only at one other plant.

THE PROCESS.

Preparation of the Batch.—The method of preparing the silica mix is the same as in other processes. The raw silica is dumped into the wet pan and 2% of slacked lime added. The batch is ground until the largest particles of silica are about the size of a pea and then shoveled directly upon a moulding table, one side of which is cut to fit the rim of the pan.

More water is used with the batch than in the old process, in order that it may more easily fill the corners of the moulds.

Moulding of the Brick.—A three-brick mould is used. The moulder simply "slops" the mix into the moulds and cuts off the excess with a wire bow. A boy then takes the mould from in front of the moulder and replaces it with an empty one. He then dumps the brick upon pallets made of lath, six brick being dumped upon each pallet. An off-bearer then carries the pallets to the drying racks.

Drying Preliminary to Repressing.—The racks which the writer used in the Utah plant were in the open moulding room, the heat being supplied from ducts under the floor through which waste heat from the kilns was conducted. Openings in the ducts allowed the heat to circulate up through the racks.

The brick are allowed to remain on the racks until they are hard to dent with the finger.

Repressing of the Brick.—They are then put through a repress. The press used by the writer was an ordinary

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Raymond Victor Repress with two moulds. The bricks are taken from the off-bearing belt and again placed upon lath pallets. The pallets are then placed in a permanent drier, where the bricks remain until bone-dry.

The attempt to repress two bricks at a time on the repress used proved a failure on account of the lightness of the springs. With a single die, however, this press gave successful results, but the capacity was cut in two. A strong heavy repress is absolutely necessary for best results. At Anaconda, a special repress was constructed on the lines of a dry press which successfully repressed two brick at a time.

By submitting the brick to this high pressure the water is forced from the interior to the surface, carrying with it the fine particles of silica. This gives a nice smooth finish to the surface, which together with the sharp corners and edges obtained in the repressing process, produces a brick of excellent appearance.

Contrary to what might be expected, the breaking, in the repress, of the bond produced by the preliminary setting of the lime does not in any way affect the final bond of the thoroughly dried ware. When the bricks are thoroughly dry, they are extremely hard, so hard in fact, that it is possible to drop them on their ends from a height of three feet without breaking them. This, of course, makes the breakage between the drier and the kiln very light.

Burning of the Brick.—The dried bricks are sufficiently strong to permit of setting to any desired height and their structure is so dense as to be sufficiently burned with a heat treatment as low as cone 9. With this heat treatment, the brick are hard enough for any purpose and have the particular advantage of being as easily cut as a soft burned fire brick.

Improved Methods of Handling the Brick.—In a plant recently designed by the writer, the brick, after being dumped upon the pallets from the moulds, will be placed directly on soft mud rack cars. As each car is filled, it

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will go into a short tunnel drier for a preliminary drying. This use of the pallet cars will save the off-bearer the trip to the racks, and will also shorten the preliminary drying period, besides putting the brick in better condition for repressing.

In the open racks, the brick were not ready for the repress for about three hours after being made, and being in the open, they naturally dried at the corners and edges first. These dry corners and edges were extremely difficult to handle at the repress. It is expected that with the use of a tunnel drier, the brick will be ready in from thirty minutes to one hour, and instead of getting harder on the outside, will dry evenly throughout.

On leaving the preliminary drying tunnel, the bricks will be run to the feeding end of the repress and, when taken from the delivery end, will again be placed upon the pallet cars. They will then go to the tunnels for the final drying, remaining on the cars until set in the kiln.

Wooden moulds were used entirely, which, of course, were sanded before filling. The writer is convinced, from observations made, that iron moulds would be far superior. The use of iron moulds with the soft mixture used would do away with the necessity of sanding.

THE COST OF MANUFACTURE.

The cost of manufacturing brick by this improved method will be approximately the same as the cost of manufacturing soft mud fire brick as practiced in the East. Each pan will produce 4000 nine-inch brick in nine hours. The total number of laborers required for the first half of the process will be one pan tender, one moulder, one mould dumper, one off-bearer and one car tender. The second half of the process will require one represser, two helpers and one car tender. This makes a total of nine men, or the same number as is required for the average soft mud fire brick gang making from 4000 to 4200 for a day's work. In fact, it will be seen at a glance that there is very little difference in the two processes.

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ADVANTAGES OF THIS METHOD.

Bricks are Denser.—It was found by actual test that the repressed brick weighed from two to four ounces more than those made by the pounding method. This means that from two to four more ounces of material are pressed into the same number of cubic inches. This can have but one result: a denser, closer grained brick, both before and after burning.

Less Heat Required.—With the brick made by the old method, it is necessary to use a very high heat treatment (cones 13 to 16), in order that the lime may become sufficiently active to bond the particles of an open body, whereas, by making the raw body denser, a lower heat (cone 9) can be used.

Brick Easier to Cut.—Brick layers often complain of their inability to cut silica brick to any desired shape, as the glassy, brittle body of the hard-burned brick will not follow the hammer. Brick made by the Anaconda method can be cut into any shape the bricklayer may wish. They are not brittle and glassy, but tough and strong. Their toughness also makes the transportation breakage much lower than that of the hard-burned brick.

Can Use a Variety of Silica Rock.—That this method is suitable for different kinds of silica or ganister is shown by the fact that the two widely varying types of rock are now being used. At Anaconda, the material used is known as a "Bull Quartz." It is a quartz rock which breaks into large boulder-like masses and is extremely hard. The Utah material is what is known as a "Sugar Quartz." It has a crystallized sugar-like appearance and is quite soft. When shot, about half of it is reduced to sand.

These materials are so unlike, physically, that there can be no doubt that the method is adaptable to different kinds of quartz.

Uses of Silica Brick.—It has long been taken for granted that the field of usefulness of silica brick is very limited, and it is, therefore, rather surprising to many to see this

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field being rapidly broadened. A few years ago it would have been thought impossible to use silica brick for boiler settings, yet this is being successfully done. For some years past, silica brick have been very successfully used for coke oven crowns and brick kiln fire box linings, two extremely hard places. Their use in the iron and steel industry is also broadening.

Machine Versus Hand-made Silica Brick.—While it would be quite impossible to get silica brick manufacturers to admit that good machine-made brick are even a remote possibility, the writer is firmly of the opinion that high-grade silica brick can and will be made entirely by machinery in the near future.

Comparative Cost of Anaconda and Old Process.—The first cost of making brick by this old method is probably less than by any other process yet devised, but considering the loss resulting from the poorer physical structure, and the greater cost of burning as compared with the "Anaconda" method, it is doubtful whether there is much difference to be found in the aggregate cost.

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SEGER'S RULES FOR CORRECTION OF GLAZE DEFECTS BY CHANGING THE BODY.

By Ross C. Purdy, Columbus, O.

On previous occasions[1] we have discussed Seger's rules for the correction of crazing and shivering. At this time we wish to present additional evidence and summarize some of the conclusions.

The new data now to be presented were obtained on white ware body mixtures of such a variety of combinations of feldspar, clay and flint, as to cover the entire field as described by the triaxial diagram.

Each body was weighed separately and the weights checked by more than one person. They were then blunged in the Bonnot jar mills, screened through a 120-mesh brass cloth, and poured into muslin-lined saggars. The slips dried and drained until the residues were in "stiff mud" condition, and when so thickened, they were wrapped in muslin and stored in a damp room for an average of about six weeks.

Materials Used.—The materials used in the bodies were Canadian feldspar, Ohio silica flint, and a clay mixture consisting of the following:

390 parts English Ball Clay No. 12.
390 " Mayfield Ball Clay.
260 " Florida China Clay.
260 " Bryson Georgia China Clay.
260 " English China Clay (unknown).

Following are the ultimate chemical analyses of some of these materials:

[1] Trans. A. C. S., Vol. VII, p. 79.

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Table 1.—Ultimate Analysis of Some White Ware Materials.

	Ohio silica flint	Canadian feldspar	Bryson kaolin
SiO_2	99.18	65.15	45.31
Al_2O_3	0.0	18.65	35.94
Fe_2O_3	0.26	0.10	0.70
TiO_2	0.01	0.0	0.04
CaO	0.01	0.18	0.0
MgO	0.01	0.0	0.0
K_2O	....	10.88	0.48
Na_2O	....	4.44	0.23
H_2O	0.11	0.32	17.00
	99.58	99.72	99.70

The Glaze.—The glaze used was:

Fritt:

$$\left.\begin{matrix} 0.1875\ PbO \\ 0.25\ K_2O \\ 0.0625\ Na_2O \\ 0.500\ CaO \end{matrix}\right\} 0.25\ Al_2O_3 \left\{\begin{matrix} 2.23\ SiO_2 \\ 0.5875\ B_2O_3 \end{matrix}\right.$$

Combining weight, 297.45

Glaze:

$$\left.\begin{matrix} 0.3\ PbO \\ 0.05\ Na_2O \\ 0.25\ K_2O \\ 0.40\ CaO \end{matrix}\right\} 0.35\ Al_2O_3 \left\{\begin{matrix} 2.49\ SiO_2 \\ 0.47\ B_2O_3 \end{matrix}\right.$$

The batch formula of the glaze is as follows:

Fritt	238.0
White lead	38.4
Feldspar	27.8
Clay	25.8
Flint	12.0

The Biscuit.—The biscuit were 10 cm. discs, made in the plastic by hand-pressing, and burned to cones 1, 3, 5, 7, 9 and 11, respectively, with coke fire in 30 to 60 hours.

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Dipping.—The bodies were dipped, using a thick glaze slip for the vitrified biscuit and a more fluid glaze slip for the more porous biscuit.

Placing.—They were placed in saggars, in stacks of five trials each, the trials being separated by stilts.

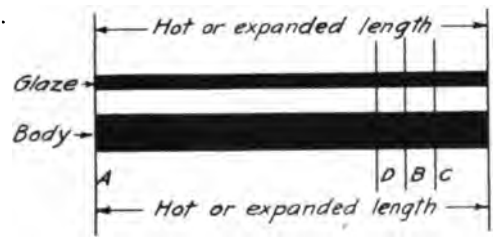
Burning.—The saggars were coke fired to cone 4 down on outside of saggars, and cone 3 down inside of saggars. Total length of burn was 50 hrs., the kiln being held at red heat for 20 hours longer than necessary for want of coke with which to progress.

The ware was cooled completely to room temperatures before drawing, ninety-six hours elapsing after completion of burn before trials were drawn and studied.

Manner of Studying Results.—The trials were sorted first by biscuit heat and then by series. The condition of the glaze on each trial biscuit was then noted on a tabular sheet.

Triaxial diagrams were then prepared for each biscuit burn, showing diagramatically the areas, and their boundaries, covered by bodies showing respectively "Fit," "Shiver" and "Craze" of glaze.

Seger Laws.—Seger's laws (as tabulated by Professor Edward Orton, Jr.) are as follows:



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Method of Control of the Relation between Body and Glaze.

1	2	3	4	5	6
Cold length of body if free to contract at will	Cold length of glaze if free to contract at will	Probable effect on the glaze	Probable effect on the body	Methods of producing these effects	Methods of overcoming these defects
AB	AB	None	None	Proper balance of all agencies	
AB — Maintaining body constantly the same, varying the glaze.	A C	Shivering	Crushi'g	1. Increased acidity 2. Replacing of SiO_2 by B_2O_3 3. Replacing soft flux by hard	Apply method given in 4–5–6
AB — Maintaining body constantly the same, varying the glaze.	AD	Crazing	None	4. Reduce acidity 5. Replace B_2O_3 by SiO_2 6. Replacing of hard fluxes by soft ones	Apply methods given in 1–2–3
AC — Maintaining glaze constantly the same, varying the body.	AB	Crazing	None	7. Reduce SiO_2 8. Add clay or feldspar 9. Use kaolin in place of ball clay 10. Use coarser ground flint 11. Softer burn	Apply methods given in 12–16
AD — Maintaining glaze constantly the same, varying the body.	AB	Shivering	Crushi'g	12. Increase SiO_2 13. Decrease clay or feldspar 14. Use ball clay in place of kaolin 15. Use finer ground flint 16. Harder burn	Apply methods given in 7–11

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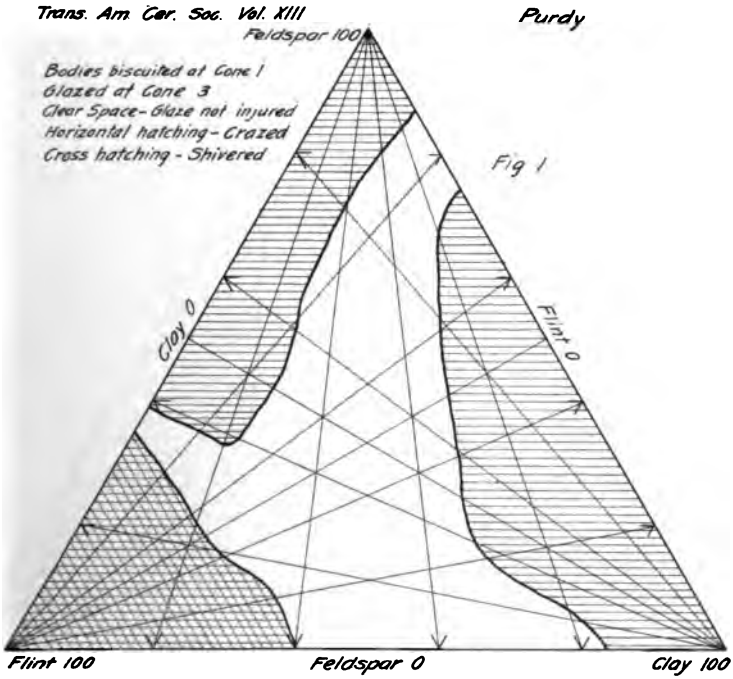
CONCLUSIONS.

(See Figs. 1, 2, 3, 4, 5 and 6.)

(1) Shivering (rupture of the body) occurred with high flint content in the body, the area of shivering decreasing rapidly as the biscuit heat treatment increased from cone 5 to cone 11.

(2) Crazing is produced by *low-flint* and *high clay*, irrespective of feldspar content.



(3) Trials with high percentage of feldspar and biscuited at cones 1 and 3 show crazing, but these same trials biscuited at cone 5 and higher showed no evidence of crazing at the time of examination. This is not in full keeping with the oft-stated opinion of practical potters that increase in feldspar in the body leads to crazing of

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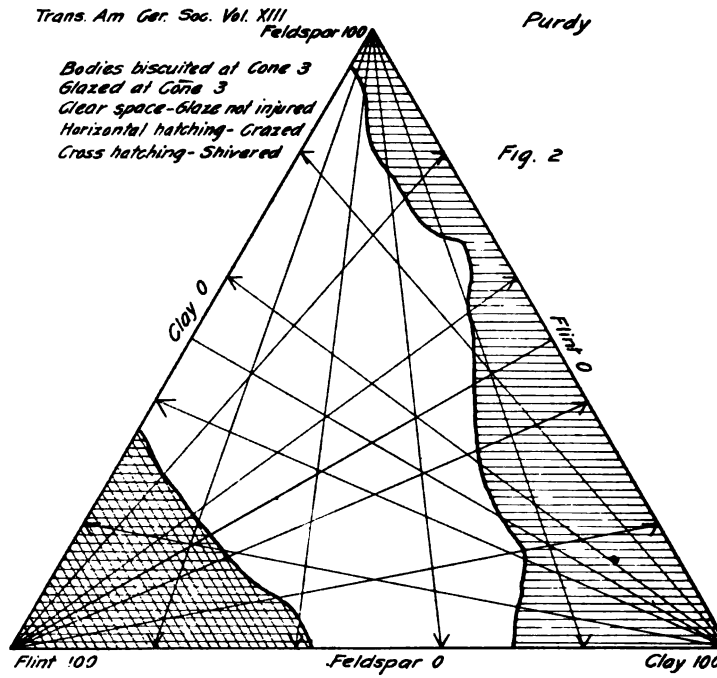
the glaze, in fact this is in contradiction to one of Seger's conclusions.

(4) The diagrams seem to indicate that with flint content between 30 and 50 per cent., and biscuited at cone 5 or higher, the bodies could have all possible variation in proportion of feldspar and clay without causing this glaze to craze, or the body to shiver under *this* glaze.



(5) **Effect of Variation in Feldspar.**—(*a*) With clay-flint proportions between (3 to 3) and (3 to 7), addition of feldspar in any quantity will *not* cause crazing unless it should do so when the feldspar content is 70 per cent. or more. Judging from the cone 5 and cone 7 glaze fit data, even this possibility of crazing, due to higher feldspar content, appears unlikely. This does not agree with Seger's rules.

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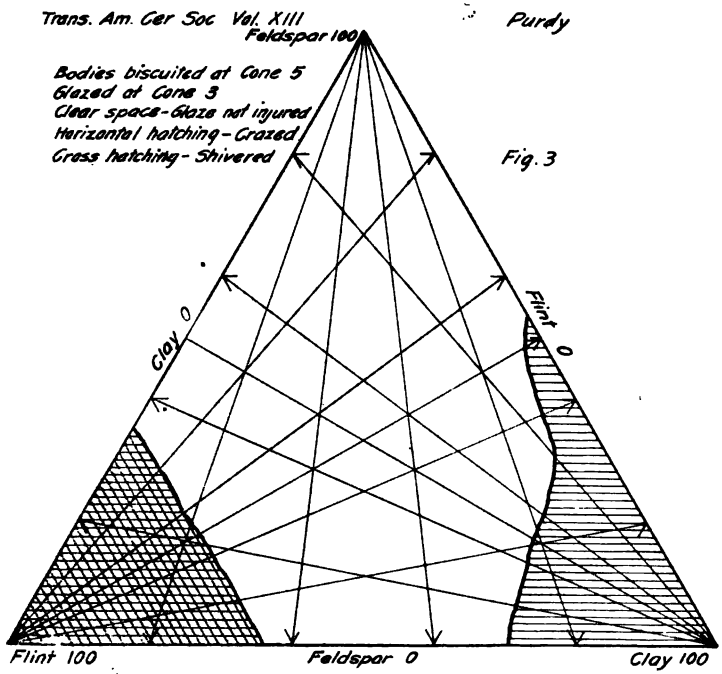
(*b*) If, however, it is assumed that Seger formulated these rules as applying only within practical limits of body variations, we find that his rule, to the effect that decrease of feldspar content in bodies will tend to overcome crazing, holds in a limited way in case of the bodies which are usually employed in china and C. C. ware, but does not hold in case of the best composition for wall tile bodies, and, in fact, in dry-pressed bodies generally.



(*c*) If, in a given body, the ratio of flint to feldspar should be changed, as, for example, from (4 — 1) to (4 — 6), the clay content remaining the same, crazing would follow *if the clay content is more than 35 per cent. of the entire body mix*, and since most pottery bodies contain more than 35 per cent. clay, it follows that in pottery manufacture, feldspar can not be substituted for flint without experiencing

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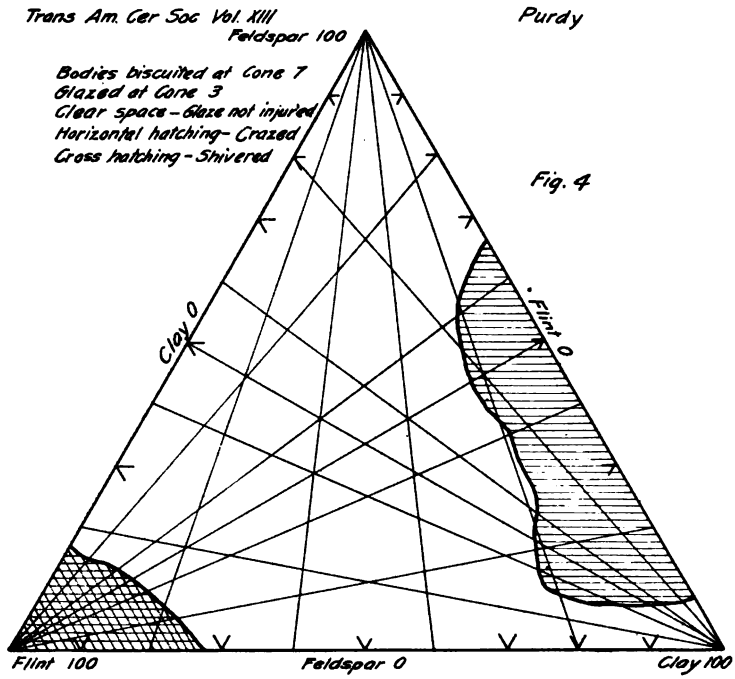
crazing. This is in keeping with Seger's rule concerning the effect of feldspar.

(*d*) In case of body mixes containing less than 35 per cent. clay, according to the available data, it may be concluded that the "glaze fit" would not be effected by change in proportion of flint to feldspar. If this proves to be the case under all conditions, then in those white ware bodies



consisting of 35 per cent. or less of clay, a change in ratio of flint to feldspar or, referring to the rational analysis, in the mineral make-up of the "clay" itself, would have no effect on "glaze fit" except when the flint should become excessively high and then shivering would ensue.

(*e*) With flint constant at 40 per cent. or more, the proportion of clay to feldspar may vary through all possible ratios without encountering crazing but with much less

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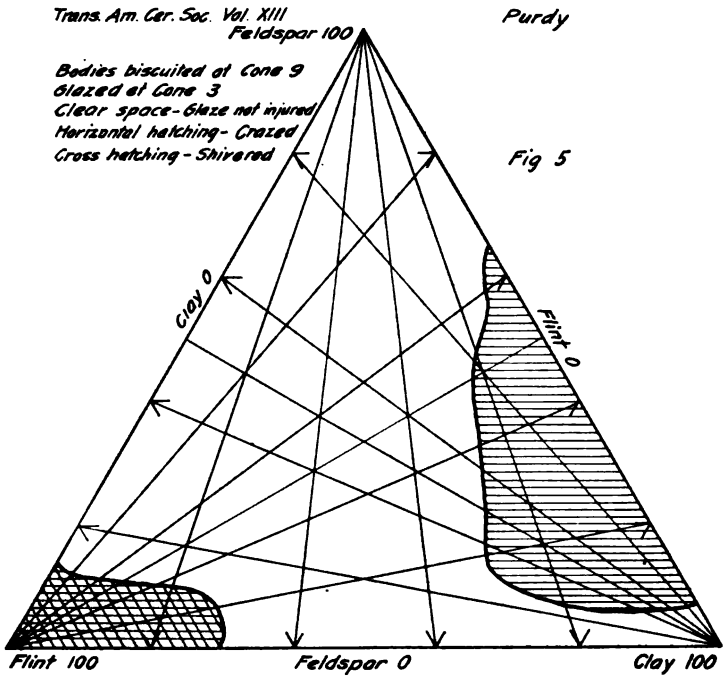
than 40 per cent. flint, the proportion of clay to feldspar on which the glaze will stand without crazing is limited to those bodies which are either high in feldspar or high in clay.

(*f*) If manufacturers would increase the flint content of their bodies from the usual 36 per cent. up to 40 per cent. or more, keeping the clay content constant, they would



find that with very little increase in biscuit heat treatment they would not only obtain ware which would be tougher[1] and whiter and less expensive, but also one which would not be effected by the changes in mineral constitution of the clays or feldspar, thus making a rational analysis (direct or indirect), without question, unnecessary.

[1] See E. Ogden, Trans. A. C. S., Vol. VII. L. Ogden, "Effect of Variation in Composition on Toughness of Porcelains," this volume.

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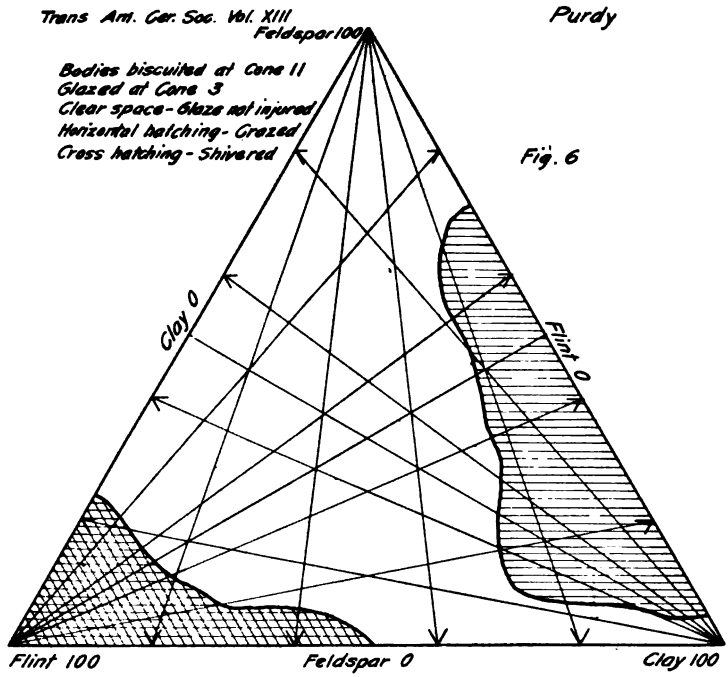
(g) *Seger's rule concerning the effect of feldspar on glaze fit applies in but few of the practical bodies unless his rule is understood to apply only to the substitution of feldspar for flint or vice versa.*[1]

(6) **Effect of Variation in Flint and Clay.**—Between the limits in proportion of flint to clay (7–3) and (3–3) respectively, Seger's rules do not apply, but outside of



these limits they most certainly do apply. In factory practice nearly all types of white ware bodies may be designed to fall within these limits, but since, for many reasons, set forth elsewhere in this volume, the practical bodies are not far removed from the boundary between the fit and craze areas, additions of clay at the expense of flint in these will surely cause crazing just as Seger says.

[1] See page 608, Vol. II, Seger's Collected Writings.

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(7) **Effect of Increase in Biscuit Heat Treatment.**—(*a*) In these studies, the crazing area *decreased* as the biscuit heat treatment increased from cone 1 to cone 7. With further increase in heat treatment (cone 7 to cone 11) the craze area *increased*, which checks Hecht's findings as shown in diagrams by Ashley (*Brick*, Sept., 1905), checking also the findings of the classes '09 and '10, Ohio State University, but which is not in full agreement with Seger's laws on this point.

Seger, according to his own admission, had no experiments bearing on the effect of increase in biscuit heat treatment (see p. 608, *loc. cit.*) but gave his rule wholly from general impression.

(*b*) Burt,[1] assuming that in his case a body fired to vitrification was "overfired," claims that increase heat treatment *up to that* sufficient to "overfire" the body *decreases* crazing. This is checked by the results obtained in our own laboratories, only insofar as some few of the bodies usually employed are concerned, but in mixtures containing more than 20 per cent. feldspar together with twenty-five or more of flint, mere vitrification will not cause the glaze to craze. In our studies, we had bodies which, when biscuited at cone 3, were non-absorbent in the 48-hour soaking test and which did not cause the glaze to craze even when biscuited at cone 11. Mere overfiring of the body or even mere vitrification will not effect crazing in all cases. In fact, the effect of increased biscuit heat treatment in causing crazing is to be seen only in mixtures containing thirty per cent. or less of flint and ten per cent. or more of feldspar.

(*c*) Burt further states that in case of "overfired" bodies (*i. e.*, vitrified) increase heat treatment *increases* crazing; therefore, Seger's law does not hold in case of vitrified bodies. We are warranted in saying that Burt's conclusion applies to very few of the body mixtures.

(*d*) Burt, in the statement that "if a body, maturing

[1] Trans. A. C. S., Vol. V, p. 342.

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at cone 6, crazes, adding silica and still firing to cone 6 will not help matters, because our body is now underfired—the body must be carried to cones 7 or 8," gives the impression that increase in biscuit heat treatment from cones 3 to 7 or 8 is more potent in overcoming crazing than the addition of silica. Our results on several body mixtures and with different clay mixtures do not check this idea. We are forced to conclude that the effect of increase in heat treatment is only slight compared to that of the increase in flint.

(*e*) Weelans[1] makes a statement that if a glaze crazes more as the biscuit heat treatment is increased, the crazing is due to overfiring of the body. Hecht's results with a porcelain glaze similar to the one used by Weelans do not check this conclusion and our results with a cone 3 fritted glaze gives clear evidence that the increase of crazing, which follows from increase in biscuit heat treatment from cone 7 and upwards, is true only for bodies low in flint (0–25 per cent.) and containing feldspar, range from 5–65 per cent. We can not believe that mere overfiring will cause all body mixtures to craze, for our glaze stood on many of the body mixtures even after they had been fired to the blistering stage.

(8) The discussion by Ashley[2] in which he points out that the same body remedies which will effect a cure for crazing and shivering with one glaze will not hold effective with all types of glazes, is very true. In fact, this is the reason for lack of parallelism in Weelan's, Griffin's and our own findings.

(9) Seger's rules can not be considered as applying rigidly under all circumstances, and at present we are not able to formulate rules that do have a general application.

(10) On comparison of results obtained by the '09, '10 and '11 classes at the Ohio State University, we find that my own conclusions[3] regarding the rather wide limits

[1] Trans. A. C. S., Vol. VII, p. 63.
[2] Trans. A. C. S., Vol. VII, p. 76.
[3] Trans. A. C. S., Vol. VII, pp. 79–88.

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of possible body variations within which Seger's rules apply, are true, but on considering all factors which effect successful production of wares on an industrial scale, I must now conclude that Seger's rules were intended to be and are applicable in certain ways only to the bodies which are usually used in white ware pottery manufacture, but either have no, or only a most general, application to those bodies which are to any extent dissimilar to these.

(11) When a potter has the opportunity to change his block and cases, and molds to allow for the difference in shrinkage caused by an increase in content of flint in his white ware body, it would be eminently wise to use higher content of flint than is generally the custom.

DISCUSSIONS.

Mr. Binns: If the area in which non-crazed ware is produced is so enormous, why do we get crazed ware at all? I noticed that on the bodies in which the flint had been replaced by feldspar, it is impossible to fit a glaze. How, then, do we glaze Belleek?

Mr. Purdy: Yesterday, I reviewed the considerations of why potters are limited in possible variation in composition of their bodies. Our craze area describes what we obtained a week or so after firing, nothing being done to hasten crazing, while Hecht's area was obtained after a longer interval, and after boiling in salts. We do not claim that ours is right and his wrong, but merely state why ours is not so badly crazed as his. The fact that he got craze in this area, which includes most of the bodies in actual use in our potteries, shows that they are liable to craze. There is no practical reason why bodies cannot be made of compositions which lie outside of Hecht's craze area, and it would be best, for as a general thing they would be too high in flint to permit of crazing.

Of course, there are special wares that could be made elsewhere. Such wares as Belleek, containing little flint, but which are high in feldspar, would be well within the

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non-craze area. Feldspar causes crazing only when substituted for flint in such bodies as are used by china manufacturers. A study of our curves will make plain the difference between the Belleek and china in this regard.

Mr. Binns: My impression still holds that if the potters would consider the rational composition of clays more thoroughly, they would avoid, to some extent, this close proximity to the danger line. Every clay contains a certain amount of feldspar, running from 0.2 to 0.5 per cent. up to 12 or 15 per cent. If you substitute a clay with practically no feldspar in it for one containing 10 per cent., you are going to increase your feldspar content and decrease your clay content. Professor Purdy merely takes clay as clay. He does not consider how much feldspar may be in it. I do not think that this is scientific. Mr. Purdy said, yesterday, although not in so many words, that it would not matter what the composition of the clay was, because the area of non-crazing is so wide; and he tried to get me to admit this. He now shows that this area is circumscribed within the realm of practical body-making, so it does matter. The content of feldspar and of clay substance in a clay is of vital importance, and I am not convinced that this is not true.

Mr. Purdy: At the Ohio State University, we have tried experiments for three different years on this rational analysis proposition, and our results were quite interesting. We took a kaolin, a feldspar, and a flint, and had our students analyze mixtures of them. When the rational analysis was reported, the figures were just the figures that we had used. Therefore, what is the good of rational analysis on a pottery body? Professor Staley was not in sympathy with me on this rational analysis proposition, and is not completely so yet; hence, he is innocent of any bias in the matter. The students are now making, under him, these same sort of analyses, and we expect they will present us with the same sort of figures. The clay will probably be equal to the clay that we weighed up, and the feldspathic

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material equal to the feldspar, and the flint to the flint that we weighed.

Mr. Binns: You are using the laboratory method with sulphuric acid?

Mr. Purdy: Yes. Furthermore, we cannot distinguish between mica and feldspar. Last year, Professor Binns said that this made no difference; that the result would be the same. I did not dispute with him, because I was content to get his statement to that effect. I am now working on some data in which I am using that quotation, but the fact is that mica will not be like feldspar in a pottery body. There is a goodly sized factor representing the difference between the two in regard to their effect on fusibility; and the German that you quoted found a similarity in general trend of the curve, but not in the data itself. The curves were not coincident. The effect of mica and that of feldspar are different, and you cannot tell how much of each you have.

Mr. Humphrey: As I understand Mr. Purdy's paper, he adopted a combination of china and ball clay, which remained constant, though the percentage varied. I should like to ask whether the results are the same, if the ball clay increases and the china clay decreases, or *vice versa?*

Mr. Purdy: We did not go into that matter, and we have not taken up the question of the difference between china and ball clay. I know, however, from Hecht's work that our areas would be different with different ratios of ball to china clay.

Mr. Burt: The subject of craze is one that the longer I live, the more I am coming to the conclusion is bigger than any we carry out experiments upon. When I started, I thought it a simple proposition; but the longer I labored with it, the more I came to believe that there is a lot concealed in it that we have not got at. I think that in a work like this of Mr. Purdy's, if he would gather what further data he could on the materials he uses, it would add a great deal of value to his paper. He should consider

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the particular degree of fineness of grain of the flint and feldspar, and possibly of the clay.

Some time ago, I advanced before the Society what I called the sponge theory. While I still hold in a large measure that change of form of the silica from its crystalline to its amorphous state is a cause of crazing, I believe there is another factor taking place that I did not think of at that time. As you approach vitrification, a greater solidification of your body, you will get a greater result from your coefficient of expansion than you would in the more porous, open structure. I endeavored to explain this by a comparison to a sponge. If you have an open sponge and push on one end of it, there is very little result at the other end. If you imagine the pottery body as a mass of open pores, you will see that it has more space in which to expand than a denser body, and the effect is not so much felt as if it were a non-porous body. In that hypothesis there is a counter-action of the theory of the passing over of flint from the crystalline to the amorphous state.

Mr. Binns: I feel that the subject is of very vital importance to the white ware men, so you will excuse me if I prolong this discussion. I would say that long ago I was entirely dissatisfied with the sulphuric acid method, but I believe in the approximate value of the calculation method of which I spoke yesterday. I believe alkali in a body, in whatever form, has somewhat the same effect. I do not think that mica has exactly the same effect as feldspar, but that its effect is somewhat the same; and that for our practical pottery purposes, it may be approximated, for the reason that mica is comparatively scarce in most body mixtures. Some kaolins contain a good deal, but the English china clay makers take the trouble to extract the mica. What mica we find approximates the action of feldspar, and I believe that we can thus ignore that factor, and by a simple method of computation, without any laboratory work at all, separate the clay into its minerals. Thus we can bring to bear our knowledge

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of the behavior of each of these ingredients, unhampered by the substance with which they are contained. Professor Purdy speaks of his experience in which a body was made up of china clay, feldspar and flint, and when analyzed, gave the same amount. The result is perfectly possible. You might find a number of instances of it, but I can also produce a number of instances to the contrary.

Mr. Weelans: English ball clay will decrease shivering, for it is high in alkalies.

Mr. Maddock: We have had crazing occasionally. It occurred before we were born, and occurs at the present time. The manufacturer may have a good body and have some pieces that will craze, and some that will not. He may drop into a run of crazing, and not get over it for three or four months; and after that, have no further trouble. Individually, I do not think that glaze has anything to do with crazing. I think that the difficulty lies altogether in the body. If you have the right body, you will have no crazing, provided that the glaze is right. As a rule, the manufacturer is in the hands of his workmen. He does not hire brains, he hires labor. They may fire the kiln one way one time, and the next time entirely differently. He has made the ware the same in each case, but the difference lies in the kiln. The man may hurry the kiln, firing it up early in the morning. He may have it fired up to the proper cone, but it has not had time enough to reach this cone throughout the kiln. If a kiln gets behind on the first day, the results will not be the same as if it had been attended to properly. The man who comes on at night cannot make up for lost time, and there will not be heat enough to penetrate to the center of the kiln, although the pyrometer may show that it is up to the proper cone. Part of the ware taken from it may be good, and part not good. I think that there is more difficulty in regard to crazing from these things than from anything else. As I have said, it is my experience that glaze has nowhere near as much to do with crazing as the biscuit itself.

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All the underfired ware will craze more quickly than will that fired up properly. With a body high in silica, you must increase the fire in the biscuit. If the body is higher in feldspar, you decrease your firing. Where the point that you cannot pass is, I cannot say.

Mr. Eleod: I was much interested in Professor Purdy's remarks that he got such exact figures in his rational analysis. I have never been able to find any feldspar in English ball clay through rational analysis, but have done so through chemical analysis. Therefore, I think that it is rather strange that Mr. Purdy should have found his figures for rational analysis agree so exactly with the way he made his mixtures. I have found that when making such analyses day after day, no two would be the same. We would always find one or more per cent. difference between the quartz and feldspar content.

Mr. Burgess: I do not think that you can take any clay as clay, the flint as flint, and the feldspar as feldspar, and mix them in such and such proportions and expect uniform results. You must know definitely what the chemical content of the various materials is, and the only way to learn is through the chemical and physical test. I may be wrong about this, of course, but I do know that when you try to substitute certain English clays for other English clays, you may produce crazing; and when you substitute English clay for American, you are pretty sure to produce crazing. If you use one feldspar for another, without knowing its chemical content, especially the percentage of soda and potash, you are going to get into trouble. I say this because I have gone through such an experience and know whereof I speak.

As Mr. Maddock has said, and as I think we all know as practical potters, a tremendous lot depends upon firing. If you do not fire the biscuit enough, you do not get the full contraction of the materials entering into that body. I think also that a good deal depends upon the composition of the glaze, but if you have a glaze that in ninety-nine cases out of a hundred comes out all right, I think that

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you can depend upon it not being the glaze that is at fault, provided you are using the same materials in the glaze. If you are using the same materials in both body and glaze, and in one case the result is satisfactory, and in the next it is unsatisfactory, there is, in all probability, something wrong with the firing. So far as crazing goes, I am satisfied that it does not depend upon any one thing, and not always the same thing, but to prevent it, requires the careful and intelligent looking after all things.

If you must change the materials, you should know their chemical and physical differences. I remember that years ago, when the old National China Clay was the best clay in this country, and we all had our mixings adjusted to a certain proportion of this clay, it began to give out. We did not know what to do and began to shift about for a substitute. Many potters tried one kind of clay, some another, but most of those who were using it got into trouble at first because of want of scientific knowledge. It happens so with almost all materials. There was a great deal of trouble in changing from the Tuscany to the American boracic acid.

This subject is so enormous that it cannot be covered in a few minutes.

Crazing depends upon various causes, and eternal vigilance on the part of the potter is the one rule for guarding against it.

Mr. Purdy: I know that you cannot substitute one clay for another without expecting a difference, but you cannot prove that the difference lies in the feldspathic material or in the chemical composition. It may lie in the content of other minerals, in difference in grain or in plasticity, and in other things that chemical analysis will not reveal. The question of fineness of grain is very important, and difference in plasticity is quite a factor.

Regarding the finding of feldspar in these mixtures to be equal to the amount that we had added, I would say that we added feldspar. If you have feldspar, rational analysis will find it; but if you have a salt of potash which

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is soluble in sulphuric acid, of course it cannot be detected in the rational analysis, and you may rest assured that it will not have the same effect as an equivalent amount of feldspar. That is why chemical analysis gets you farther from the facts than rational analysis.

In reply to Mr. Burgess, I would say that if he has been using a body containing the same percentages of clay, feldspar and flint as used by the large majority of potters in this country, I am not surprised that a small difference in character of the body ingredients would be apt to bring on crazing, for the majority of the pottery body mixes are very close to the craze area. I have shown how the potter may so compound his bodies as to greatly lessen this liability to craze.

Mr. Parmelee: Mr. Stull has raised the point that crazing may be due to other things than a difference in the coefficients of expansion, and has suggested crystallization as a cause. I want to ask Mr. Purdy whether he has noticed any difference in the craze line in his glazes; for instance, the circular line accompanying the separation of crystals?

Mr. Purdy: I have found circular lines and straight lines, but no crystals. A craze was a craze to us. As to the cause of the crazing, we have not gone beyond finding that it is caused by a change in composition. I do not wish to go on record as supporting any theory which has been advanced concerning the cause of crazing. I have confined my remarks wholly to observations and to deductions which were too obvious to require either development of new things or the support of those already advanced. My work is exactly of the same order as could readily be executed by any potter who would take the trouble to make such extensive studies.

Charles Weelans: This contribution is a very valuable one; its thorough and exhaustive treatment carries us further into the subject than we were wont to go. It seems to prove that some of the statements of former writers upon this subject were not wholly correct, due as

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Prof. Purdy says in a great measure to the narrower limits of their research, they confining themselves more to the work of bodies and glazes of practical composition.

A hasty review of Prof. Purdy's work will not permit of a lengthy discussion yet we would like to observe that while it seems to be in contradiction to much that has been said before, in many instances it is a corroboration of them. Herein is the work valuable, for it eliminates the weak points of other arguments and strengthens the strong ones. Prof. Purdy's evidence even though preliminary, "That pottery bodies containing less than 35 per cent. of clay would be proof against crazing irrespective of the proportion of flint to feldspar," should be helpful to the pottery manufacturer, especially to those of limited knowledge and experience. We cannot so heartily concur with Prof. Purdy's statement apparently recommending that "If manufacturers would increase the flint content of their bodies from the usual 36 per cent. to 40 per cent. or more, keeping the clay content constant, they would find in a very little increase of biscuit heat treatment that they would not only obtain ware which would be tougher and whiter and less expensive," etc. The qualities of toughness, whiteness and expense are important qualities, but in successful pottery manufacture there are so many other conditions of even greater importance that the above qualities, to a considerable extent, must be subordinated to them.

We consider it hardly advisable in ordinary earthenware manufacture to use so high a content of flint as 40 per cent. or over. In the manufacture of earthenware the many dangerous elements entering into it are not always under control. It is fired generally in kilns of large diameter, and an even temperature is not always obtainable, and however safe the above recommended body composition might be in the higher temperature of the kiln, for the lower temperature it is too near the danger line. Good clay in and out of kiln is the thing most important to the earthenware manufacturer, and the body composition

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that will most successfully meet the sometimes uncontrollable conditions of manufacture; that body which affords the greater margin of safety between shivering, crazing and cracking is the most acceptable.

These remarks are made presuming that Prof. Purdy in his recommendations was referring to earthenware bodies and not china bodies.

Another conclusion stated later; namely, "In these studies the crazing area decreases as the biscuit heat treatment increases from cone one to cone seven, and that in further increase of heat treatment—cone seven to cone eleven—the craze area increases," is in perfect accord with many other writers, presuming that the body used reached its maturity in the lower heats and became overfired in the higher heats. However, Prof. Purdy modifies this statement later when he says, "Mere overfiring of the body or even mere vitrification did not effect the crazing in all cases."

In practice generally, the first statement is found to be true, crazing in the overfired bodies ceasing only when the glaze is changed to suit the overfired body, although this glaze when so changed would not be so satisfactory where the body has received proper treatment.

Following this in Prof. Purdy's conclusions, he refers to the following statement made by the writer: "If a glaze crazes more as biscuit heat treatment is increased, the crazing is due to overfiring of the body." Prof. Purdy finds in "Hecht's Results," the contradiction of this and also apparently contradicts it himself by stating that he fired some of the bodies to the blistering stage and found no craze. In answer to this I would say that the writer did not say that all glazes would craze with increased heat treatment of the body, but in such glazes as the writer was then using in his experiments.

As an evidence of this truth, I would refer to a paper read by the writer at our Birmingham Meetings ("American Transactions," Volume 7, pages 57 and 58) from which I quote the following: "It was the writer's intention, origi-

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nally to overcome the crazing in these high-fired pieces by changing the glaze as had been done many times in practice, but time would not permit this."

Again, the writer cannot wholly agree with Prof. Purdy that "blistering" is always an evidence of overfiring. We have had, in practice, many cases of blistering body where the body was underfired. Again, the highest temperature Prof. Purdy used in his work (if the extract now in the possession of the writer rightly states) was hardly sufficient to overfire many of his bodies. The heat the writer used in the work, which occasioned the above statement of the writer and to which Prof. Purdy referred, was as high as cones fourteen and fifteen, and it was in *these increased heats* that the writer secured the results spoken of.

If an earthenware body reaches its full maturity at cone seven and the glaze used be fitted to mature at or about the same temperature, overfiring of the body is likely to bring about crazing; but in a porcelain body requiring much greater heat to bring it to maturity, the same glaze may be used with *less* liability to crazing. On the other hand, if an earthenware body, maturing at cone seven, be overfired, using a glaze though bright at cone seven but through its wider range is enabled to withstand a much greater heat without damage, the liability for crazing in the overfired earthenware body is less. For this reason we are, by changing the glaze, enabled in a measure to free the overfired body of this fault of crazing.

NOTE PREPARED AFTER HAVING READ THE PAPER.

Mr. Burt: This paper, while treating in part, with mixes far from practical, also aims to cover the parts in which practical working mixes would be found. The remarks here given are from conclusions drawn from practical mixes only.

Test Pieces.—Purdy's bodies were "blunged in jar mills." Blunging, to my mind, is never grinding, while a jar mill always gives more or less grinding. Grinding

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often makes all the difference between craze and shiver. After drying to "stiff mud," in manner described, thorough pugging, which is very necessary, is not mentioned.

Test pieces made in the plastic by hand-pressing give a very poor trial to judge general results, because, first, the variations caused by the individual presser; second, lack of uniformity due to the face and sides being forced against the plaster while the back is not; and, third, the variation between results from same mix whether pressed or cast. All potters know that the same mix may shiver when pressed and craze when cast.

Cause of Crazing.—The chart method of showing the effect of body changes on glaze fit is new and very interesting, but after studying it and the late researches in coefficient measurements, I still hold to the old theory that crazing and shivering are due to varying coefficients.

Let us imagine a fully fused glaze on its body at full heat. Any difference between the two in this condition is easily adjusted because of the plastic state of the glaze. If, after cooling has progressed to a point where the glaze is no longer plastic, the body and glaze do not contract alike, strains will be set up from the time the glaze begins to harden, and continue to increase in severity as the cooling proceeds.

Purdy claims that Seger is inconsistent in describing crazing as an effect of the glaze having the higher coefficient of contraction on cooling if he does not grant the possibility of shivering in the same glaze due to the higher coefficient of expansion of the glaze on heating (see Purdy and Potts on "Influence of Clay, Feldspar and Flint on Coefficient of Expansion of Certain White Ware Mixtures, Biscuited at Cone 10"). I claim that Seger is not inconsistent, for I hold that both crazing and shivering are due to strains which start with the fixing of the glaze and grow worse as the cooling proceeds. Reheating merely reduces the strain.

Few pieces come from the kiln free from strain. If the glaze has the greater coefficient of contraction, it will

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be put under a strain in trying to cover the body, and presently, if it has not sufficient elasticity to longer stand this strain, crazing will result. If the conditions should be the reverse of this, that is, if after solidifying, the body should contract more than the glaze, the glaze would push off, *i. e.*, shiver.

I offer the following comments, seriatum, on Purdy's conclusions.

(1) High content of uncombined flint will result in high coefficient of contraction of the body which, quite naturally, would cause shivering.

(2) Low flint and high clay would give a body a low coefficient. Feldspar itself, being of low coefficient of contraction, does not affect the results except in so much as it dissolves the flint.

(3) There is no doubt but that in many mixes an increase of feldspar at the expense of flint is the surest way of causing the glaze to craze.

Purdy, commenting on my statement that overfire caused crazing, remarks that this was not true of bodies with over 20 per cent. of feldspar. I confess that I was speaking of practical bodies and I know of no pottery or tile bodies in use containing over 20 per cent. feldspar. Purdy grants my statement true for mixes of less than 20 per cent. feldspar, and then goes on to say: "We are warranted in saying Burt's conclusions apply to very few of the body mixes."

Pottery bodies and tile bodies do not vary to any great extent as the majority may be found between 50–55 clay, 10–15 feldspar, and 35 flint. Now these are usually not fired to vitrification and Purdy grants my contention that increased fire decreases crazing up to full vitrification and does not disprove the further statement that with vitrification of these bodies crazing will increase. Seger not only worked with these so-called pottery and tile bodies but also with porcelain in which the feldspar is 20 per cent. and over, so that his general statement may be too broad.

In my statement that increase of flint without increase

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of fire will not help matters, we have another case of too broad a statement. It is true that increase of flint will, at the same heat, give less crazing if this is done with a hard fired ringing body; but the danger of increase of flint without increasing the fire is, as was well brought out by Weelans, Maddock and Mayer, that it would produce dunting.

In considering this valuable work of Mr. Purdy, generally, the main impression left is that of the amazing complexity of the problem. He is dealing with one clay mix varied with flint and feldspar through varying heats under one glaze.

Starting with clay, we know that under a given glaze one clay seems perfect under all conditions, while another crazes and still another shivers even with no admixture of flint and feldspar. This comes in terra cotta bodies which now have to be glazed. Expense prohibits flint and feldspar, so what is to be done to adjust these bodies?

Fortunately, the low coefficient of the average kaolin does not have to be used as nature has provided shales and fire clays which not only hold glazes far better but give better bodies. If Purdy, instead of testing his given clay mix had taken Mayfield ball clay alone, he probably would have had shivering instead of crazing which he tells us comes from high clay. With Florida china, the result would have been bad crazing. Then again, stoneware potters will tell you that Albany slip glaze will not craze on any clay.

He uses Canadian potash feldspar. Had he also tested soda feldspar, he would have found that the mixes which craze with the potash would have shivered with a soda feldspar.

He doesn't give us any data on the fineness of his flint yet that which would just pass 120 might give a crazing body, while the same mix could be made to shiver if the flint easily passed 200.

His trials are 10 cm. discs which are no criterion of

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what effect these same variations in body would have on large pieces.

Most clay wares are made wet but the tile maker uses damp dust. The tile made from stiff mud may give a fine fit while the same mix as dust-pressed tile would possibly craze. Then, too, the degree of fire is all important. Purdy doesn't seem to think so, but it is painfully true in glazes as well as in bodies. As I stated some years ago, an underfired glaze is the worst sort to craze.

One could go on citing factors in this complex problem but these few should show that Purdy must be careful to apply to himself the criticism he makes of Seger and not draw broad conclusions. He makes the same criticism of my conclusions of some eight years ago, and he is, in the main, right, and I realize that we can hardly be careful enough in stating that results given apply only to certain clearly stated conditions.

However, I do believe all should be allowed to theorize, in fact, encouraged to do so. Seger gave us the coefficient of expansion theory to explain crazing and shivering. This seems to me the most probable one so far advanced.

The question might be asked, How can terra cotta be fitted with a glaze if made from clay only, while elsewhere we speak of clay as the great source of crazing? Again, it is too broad a statement. Kaolin, pure, with no free flint, is a great cause of crazing, because of its low coefficient, but the shales and fire clays carry more or less free flint and, almost equally important, fluxing impurities. It is these fluxes which cause the clay, at comparatively low heat, to fuse to a hard firm body. It is this fusing of the body that develops the higher coefficient, and naturally the more free silica present, the higher it will be, provided the silica is finely divided.

Take a mix of a 50 raw fire clay and 50 of the same clay, fired and ground coarse for saggars, and glaze it: you will probably have bad crazing. Take the same clay, the same mix, but ground finer and glaze

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with the same glaze, there will be much less, if any crazing. Coarse and fine flint will make this same difference. This, I claim, is due to the physical character of the body. The open porous saggar has low coefficient of expansion, owing to the expansion being largely absorbed in the pores, while fine mix is closer, having less pore space, hence, as a whole, greater expansion. The coarse saggar can stand sudden temperature changes, when other mixes would dunt; so the terra cotta maker seeks a clay which contains fine flint and fluxes sufficient to give a hard body at as low a heat as possible. The clay must, of course, at the same time satisfy all other necessary conditions.

Does this not throw some light on the feldspar and white ware problem? As I gather from Purdy's paper, he claims to show that feldspar is not as bad as it is painted by potters generally. Insofar as the feldspar serves to aid in fusion, that is, forming of a closer knit body, I believe it does aid in developing what I call latent coefficient. In fact, this is what increased fire does, and feldspar, undoubtedly, assists this action. I have tested this by adding a small amount of glaze fritt to a crazing body, rendering it much harder and thereby free from crazing. The same is true of the use of soda feldspar. Its greater fusion gives closer bodies and reduces crazing. As Purdy says, however, the increase of feldspar must come at the expense of clay and not of the flint. With this in mind, I have lately tested a raw lead glaze of fairly high coefficient on a piece cast from a mix of 30 clay, 30 feldspar and 40 flint, which was fired in the biscuit to almost complete vitrification. I confess that it was to my surprise, to find apparently a perfect glaze fit.

Great need of all glaze ware is a large margin of safety, that is, range in which the glaze will fit. The surprise to me in these charts is the great field claimed for glaze fit. My practical experience has never shown this. In other words, the range between shiver and craze is not nearly as great as shown.

It is an impossibility to fire a big kiln with absolute

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uniformity, and frequently the range of heat alone is sufficient to upset glaze fit.

The least variation between shipments of raw material may throw out your glaze fit. Our margin of safety is too narrow. We want to be helped not only to the best fit but also to the most elastic one. This paper of Purdy's certainly throws very interesting and valuable light on the field he has investigated and following his suggestions may carry us nearer the desired end.

NOTE PREPARED AFTER HAVING READ THE FOREGOING DISCUSSION BY MR. BURT.

Mr. Purdy: I am in accord with most that Mr. Burt has to say in criticism of the manner in which we prepared our biscuit trial pieces, with one exception, and that is in the implication that we were not aware of the fact that the manner of formation of the ware had something to do with the control of glaze fit. I ask that it be remembered (1) that we described in detail the manner in which the trial pieces were made, (2) that in an investigation of this extent we necessarily have to limit the number of variables, and (3) that no matter how unlike factory practices our methods may have been, we obtained results that checked those of Hecht, and those obtained in our class work during the last few years, and (4) that they agree remarkably close with those I obtained on dust-pressed biscuit trials.[1] I make no justification of the method we used except that of expediency.

Messrs. Walker and Mayer[2] reported a case of a glaze behaving differently on a dry-pressed tile and on ware made in the plastic. I wish to draw attention, however, to the fact that the trouble here was not in glaze fit, but in production of equally good glazes on each of the two bodies. I have some dry-pressed biscuit tile which I warrant 99 out of 100 glaze makers could not cover with a glaze even on the second or third trial. Why this is, I do not

[1] Trans. A. C. S., Vol. VII, p. 91.
[2] Trans. A. C. S., Vol. II, p. 158.

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know, but I do know that I did not succeed in glazing it in the first three attempts. On this biscuit, most glazes disappeared entirely, the tiles coming from the glost burn having every appearance of never having been in contact with the glaze.

I have never had experience with a glaze and body combination that would shiver when pressed, and craze when cast, although I have made a variety of bodies and glazes, using them indiscriminately in the one way or the other, and this, too, without any thought of there being a difference in glaze fit under these two conditions. This statement by Burt is a surprise to me.

We know full well that some glazes permit of a wider latitude in conditions when being fixed onto a body than others, and it is reasonable to expect, as Hecht found, that the glaze fit area will be much narrower, that is, the craze and shiver areas will be much closer with some glazes than with others. I have spoken of this before.[1] The problem of determining in what way variation in composition of the glaze affect these differences in glaze fit was considered by Fox and myself[2] but it deserves a much more thorough investigation, for in our laboratory work we have found glazes that would craze on any and all bodies on which they were tried, and within the full range in variation of glost heat treatment which the glaze would permit. This sort of behavior of some glazes is puzzling to me. None of the theories of crazing seem to give satisfactory explanation. I can well imagine, therefore, that a potter who attempted to work with a "short range" glaze may experience shivering on pressed ware, and crazing on cast ware, even when using the same body and glaze in both instances. It seems to me, however, that in pottery experience this would be an exception rather than the rule.

Cause of Crazing.—Mr. Burt reaffirms his belief in the theory of crazing as set forth by Dr. Seger. I will

[1] Trans. A. C. S., Vol. VII, p. 80.
[2] Trans. A. C. S., Vol. IX, p. 95.

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attempt to show that the statement by Dr. Seger, as well as that of Burt's, really confuses two wholly different physical factors, the one being that of strains produced between the glaze and body in cooling, and that of difference in coefficient of expansion and contraction.

Seger,[1] under the general topic head of "Chemical and Physical Relations between the Composition of a Body and Glaze," speaks first of the coefficient of expansion, not only of bodies and glazes but of other materials as well. In this same paragraph, he speaks of the strains produced when the ware is cooling. In the next paragraph, he again refers to both of these physical factors (strains set up in cooling and difference in coefficient of expansion of the cooled body and rigid glaze) devoting to each, one sentence. This paragraph reads as though these two possible causes of crazing are not necessarily interdependent.

In the first sentence of the last paragraph, on page 573, and throughout that paragraph, it becomes very plain that he is considering only one of these physical factors, *that of stress set up between the glaze and body in cooling*, and is merely incorrectly applying to this difference in contraction, this same expression which, for decades, has been applied to differences in rate of volume change at ordinary atmospheric temperatures.

That Seger is really holding these strains which are set up when the glaze is becoming rigid, as the sole cause for lack of glaze fit, rather than any difference of coefficient of expansion and contraction there may be between the two after having cooled, is made plain by the paragraph on page 574, which reads:

"Through this difference in the contraction while cooling, but always only after the complete hardening of the glaze, a set of phenomena are produced whose most intimate study is very important for the technology of the clay industry, and it seems appropriate to give the results of a series of exact scientific researches, carried

[1] The collected writings of Herman A. Seger, A. C. S. Translation, Vol. II, p. 572.

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out on this line, without, at this time, giving the details of such an investigation."

A careful study of the last paragraph, on page 574, and the first three paragraphs on page 575, makes plain to me that he sadly confused these two physical phenomena by merely incorrectly using the expression, "coefficient of expansion and contraction." I feel sure that the idea he wished to convey in the last paragraph on page 574 and in the succeeding one is that to measure the volume changes, which a glaze would show when cooling, would be futile for this would fail to take into consideration the conditions under which the glaze on the ware is cooled, the change in composition, due to the solvent action of the glaze on the body, the sinking of the glaze into the pores of the body, etc., etc.

I am going to ask Professor Bleininger to read, in the original, this part of Seger's article on "Defects of Glazes," to see if it agrees with our English translation. It is, indeed, difficult for me to believe that Dr. Seger would be so careless in the use of the expression of "coefficient of expansion and contraction" or of so badly confusing these two distinct physical phenomena, as is apparent, not only from the subject matter of the text, but also from the fact that the two are frequently mentioned together in the same paragraph.

If, when speaking of coefficient of expansion, etc., Seger referred to strains due to the difference in volume changes in glaze and body on cooling after the glaze had become rigid, then our statement, to the effect that the difference in actual coefficient of expansion and contraction of the body and glaze has very little part in causing crazing, is not at all out of harmony with what Seger has said. If my present interpretation of Seger's statement is true then there would be no great difference in fact between Staley[1] and Seger.

If this interpretation of Seger's views is *not* correct,

[1] Trans. A. C. S., Vol. XII, p. 322.

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then I claim we were justified in the charge that Seger was inconsistent unless he would grant that when a glaze had the higher coefficient of expansion and contraction, it would be just as apt to shiver when heated, as it is to craze when cooled.

Mr Burt's reply to this claim is plainly unsound, for it does not require a careful study of his words or of his rhetoric to determine whether or not he is confusing the volume changes which a glaze experiences when cooling with the volume changes which it would experience when subjected to ordinary temperature changes.

It would be too long a story to recite the known instances of very decided changes of volume in minerals at definite temperatures due to change in crystalline form, and it would be altogether too absurd to attempt to prove that in our glazes there are compounds formed which suffer these volume changes. I will mention the fact, however, that several investigators have proven beyond question that wollastonite is present as such in window glass[1] and geo-physicists have determined[2] that this mineral suffers an inversion at about 1180 degrees centigrade, but that the temperature at which this inversion takes place is conditioned by the composition of the magma from which it would crystallize and, further, that when this inversion does take place, it suffers a change in volume. We have heard much of the slow inversion of quartz to tridimite at 800 degrees centigrade, in which it suffers a volume change of about 12 per cent.

If there is fact in the theory of crazing which Staley gives, and which I believe that Seger and Burt really have in mind, one might ask us to justify the claim that flint added to a glaze tends to overcome crazing. I would answer, in the first place, that addition of flint to a glaze will not always cure crazing, and, in fact, the mixtures have been many in my own experience in which crazing could be cured only by de-

[1] W. Jackson and E. W. Rich, Jour. Soc. Chem. Ind., 1901; K. Zulkowski, Chem. Ind., 22 (13), 280; Jour. Soc. Chem. Ind. (1891), p. 464.

[2] Allen and White, Am. Jour. Sci., Vol. XXI, 122 p. 100, 4th series.

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creasing the silica content. On this subject I am now preparing a paper for presentation at our next meeting. I would answer the question further by citing an instance in which addition of SiO_2 to a mix tends to counteract the volume changes which, in glazes, may cause these strains, resulting, finally, in crazing or shivering. In the cement manufacture they have a phenomena known as "dusting," that is, the fused clinker, without application of external force, will crumble to powder. It has been demonstrated that this is due to the inversion of Ca_2SiO_4 from the alpha to the rho crystalline form involving a considerable volume change. The addition of silica to such a mixture will check this tendency to dust. If silica be added to Ca_2SiO_4 in amount sufficient to make $CaSiO_3$, in place of the orthosilicate of calcium with its large inversion volume change, we would have wollastonite which has a much less volume change. Silica may have somewhat the same effect in glazes.

I have indulged in the foregoing recitation of facts to show that in advancing a theory for crazing, its cause and cure, there is no need of the fallacious argument that in glazes the SiO_2 is in the amorphous state and, therefore, it reduces the coefficient expansion of the glaze. Such an argument is entirely out of harmony with what has been learned in geo-physics.

I cannot conceive how, with a "long range" glaze such as we used, and with a given percentage body mixture of clay, feldspar and flint, we could go from crazing to shivering by merely changing the clay of the body. In our work we have experimented with nearly all of the English and American clays which are used by the American potter, and have yet to see a case of this sort. In the vernacular of the street, "You will have to show me."

As to the effect of "degree of fire" would say that I referred altogether to the biscuit fire. If Mr. Burt had been here when we put two wheelbarrow loads of tile direct from the glost kiln to the dump because the glost heat was too low, he would know how careful we were that our trials should all receive cone 3.

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I am content, even after reading all these discussions, to let my conclusions stand as first presented. I ask that the work of Dr. Hecht, as presented by Ashley, in this volume, be carefully studied, for in that work will be found refutation to most all the adverse remarks concerning "the great field in which the glaze fits."

Mr. Burt: Mr. Purdy is right in saying that I am confusing the volume changes which a glaze experiences when cooling with the volume changes which it would experience when subjected to ordinary temperature changes, "provided he realized what I definitely state," *viz.*, these volume changes are after the glaze has ceased to be plastic, that is, has become rigid. If he knows of cases in which "very decided changes of volume, due to change in crystalline form," have occurred after the glaze has cooled to rigidity, I would be glad to hear of them. He cites the inversion of quartz with its volume change; this, and like phenomena may occur and may be important factors in the question of glaze fit but do not bear on the point under contention. As I see it, the question is, given a glaze cooled to fixity, does it contract on further cooling? If so, can this contraction be measured by a coefficient of expansion and contraction? I fail to see why not, nor what difference it makes whether we consider it as contracting from 800 to 100 or from 100 to 0. Does expansion and contraction of glaze and body only occur at ordinary temperatures?

It hardly seems probable that Seger would have confused the "strains which are set up when the glaze is becoming rigid with the strains from cooling after glaze had become rigid."

Seger was no great believer in matt glaze, but any one working with different matts, showing greater or less crystallization, soon finds such varying results from those obtained with clear glazes in respect to glaze fit that he is soon convinced that a new factor has been introduced. I theorize about these crystalline matts that while a clear amorphous glaze goes into a rigid state probably free from

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strain, these matts, owing to crystallization continuing to point of rigidity, are probably under a strain when they reach the rigid state. Once rigid, however, does not both the glaze (clear or matt) and body begin to contract? The papers cite a case of expansion at extraordinary heat. Cleveland has just had the hottest weather in 40 years. It is a great place for vitrified paving brick. During this hot weather, two cases were given where the expansion was so great that the street was buckled up until finally the brick were forced up into the air.

Let us consider volume changes from other causes, certainly, but let us not throw overboard those caused by heat until Mr. Purdy has given more proof.

Mr. Weelans: Concerning Mr. Purdy's experience that the addition of flint to a glaze will not always cure crazing, I would like to ask: "Do we not pay too little attention to the part the temperature, at which these glazes are fired, plays in these varying results?" If a glaze fired at cone 7 has ten or more per cents. of silicate than would be warranted at the temperature used, would it not be natural that if the glaze should craze an *increase* of flint would be the remedy? On the contrary, if the glaze had 10 or more per cent. flint more than such a temperature would warrant, and the same fault of crazing resulted, would not a *reduction* of the flint be the remedy?

We have had glazes craze:

(1) From too much flint, and

(2) Too little flint for the temperature used, but at a suitable temperature for each, both glazes would stand.

I would further add, in connection with shivering, that it is hardly possible to determine at just what point most bodies will shiver unless we make up large, heavy pieces and make them up in various forms. We have had bodies entirely free from this fault in one of certain forms, but when made in other forms, these bodies, fired in the same kiln, would be wholly bad from this fault. We have, therefore, stamped these bodies as "shivering bodies," yet were we making these certain styles or forms of ware

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as above in which this fault did not appear, we might never have had cause to abandon them.

NOTE PREPARED AFTER HAVING READ THE DISCUSSION OBTAINED AT THE MEETING.

Mr. Purdy: The foregoing discussion concerning the value of rational analysis consists most largely of mere expression of opinions, very little of material evidence being presented. Since Professor Binns is the chief exponent of the calculated rational analysis, we may look to his formal paper[1] on this subject for this evidence.

I intend to challenge most of his premises and prove that his conclusions are not substantiated by the data he presents.

At the outset, I want to make plain that I agree with Professor Binns as to lack of accuracy in the old rational analysis. I would go still further and maintain that the results obtained in this analysis have no more value than would similar data empirically assumed. For proof of this, I refer to the use Dr. Seger made of the rational analysis of the Japanese porcelain. After having the data from this analysis, he proceeded in the old cut and try manner until he obtained the desired results, but the mixture which gave these results were far different from that which, by rational analysis, he supposed the Japanese porcelain to be. I could refer to my own laboratory notes for illustrations of this same sort from attempts to duplicate certain floor tile bodies. *The data from rational analysis has not as much value as has empirical data taken from experience.*

Admitting the inaccuracy of the rational analysis and implying its want of value, Professor Binns urges the adoption of a calculated rational analysis based on the assumption that the alkalies in a clay may be taken as an index to its feldspar content. When formulating premises on which to base his arguments, his first inquiry

[1] Trans. Amer. Cer. Soc., Vol. VIII, p. 198.

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was: "Is kaolinite or clay substance, having the formula $Al_2O_3.2SiO_2.2H_2O$, always the same, except for such variations as may arise from relatively coarse or fine grain, and how far does the difference in grain affect the behavior of the clay?"

Kaolinite *is* always the same except for such variations as may arise from size of grain, *but* kaolinite and clay substance are two distinct things, the difference being of the same sort as between silica sand and sand. I hold with Ashley and others that the clay substance, the substance which gives clay its characteristic properties, is properly defined by the nomenclature used in the mechanical analysis, *i. e.*, clay substance is the finest portions of the clay whatever its mineral nature may be. To be specific in this argument, however, I challenge Professor Binns to prove that 75 per cent. of a china clay is kaolinite. Take for example, Georgia kaolin, the composition of which is nearly the same as that of kaolinite. I doubt very much if he can show that this kaolin is largely kaolinite.

He admits inability to identify the minerals in ball clays.

Concerning his second premises (page 203), would say that I am indeed surprised to hear Professor Binns claim that the alkalies will have the same influence, whether they be present as soluble salts, or as constituent part of minerals. The only reasonable objection that can be made to the molecular formula of glazes is that they do not indicate the source of the oxides. There is such a unanimity on this point I need not dwell on it further than to cite a case.

One of our students had arrived at the conclusion that in fritted glazes there was no need of considering the source of the various oxides shown in the molecular formula. He made up a series of frits, all alike in molecular composition, but each differing in the raw materials used. These frits were mixed in the same proportion with the same raw materials. Each frit and each glaze were given the

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same treatment throughout, but the resultant effect of each frit was very noticeably different. *The alkalies introduced into glazes as a constituent part of a frit have very different influence according to the difference in their source.* This being so, how much more difference in effect could be expected from difference in the state or kind of combination of the alkalies in a clay?

Professor Binns will have to demonstrate synthetically or otherwise that alkalies have like effect no matter how present in clays before he can claim that this, his fundamental premises, is correct. If he succeeds in doing this, he will have findings that will be out of harmony with those of Iddings and his fellow geo-chemists.

I ask Professor Binns to show that his argument or premises are in harmony with Weber's[1] results which show the lack of relation between alkali content and refractoriness of clays, and with failure of Hoffman and Desmond[2] in their attempts to devise an indirect method of determining refractoriness of fire clays. I would further ask Professor Binns to show why fire clays that have like chemical composition have unlike rates of vitrification. If there is much of fact in his premises or of value in his method, he would not find difficulty in explaining these. They cannot be explained on difference in fineness of grain. This I have very adequately shown.[3]

Professor Binns has not as yet made answer to the criticism of his assumed premises made by Dr. Ries[4] three years ago. This should be done.

Are Professor Binns' conclusions substantiated by the data offered?

The data he offers were obtained with the following clays and mixtures. He made five bodies, using in each

[1] Trans. Amer. Cer Soc., Vol. VI, p. 222.
[2] Trans. Amer. Inst. Min. Engr., Vol. XXIV, p. 32.
[3] Geol. Survey of Ill., Bulletin 9.
[4] Trans. Amer. Cer. Soc., Vol. IX, p. 772.

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a different clay, all being so compounded that, according to his analysis, each was supposed to contain:

Clay substance	65
Feldspar	20
Quartz	15

The mixture of materials were as follows:

Clays used	English ball	Edgar's Florida ball	Tennessee ball No 1	Delaware kaolin	Georgia clay
Per cent. clay	87.2	63.55	77074	69.01	63.34
" feldspar	7.91	25.57	16.60	19.84	26.20
" flint	4.97	10.91	5.70	10.12	10.12

His first observation is: "It will be seen that in this series of bodies there is only one variable, the clay substance, and that this is a variable only in the physical form. Thus all the changes observed in shrinkage and in coefficient are due to this factor alone. It must be admitted, however, that the variation in physical form goes a little farther than clay substance itself, for, while the flint and feldspar in the respective mixtures were finely ground, it is probable that the quartz and feldspar in the clays were finer still."

How he came to the conclusion that in this series, clay substance is the only variable, is beyond my comprehension, unless he had in mind that what he calculates as feldspar and flint is *not* feldspar and flint. He does not make this plain, in fact, he says: "While the flint and feldspar in the respective mixtures were finely ground, it is probable that the quartz and feldspar in the clays were still finer." And later: "Is all of the alkali in clays due to the presence of undecomposed minerals. . . .? The presence of alkali in the soluble portion of a clay does not alter the fact that it came originally from these minerals. . . . . In other words, there is no reason for supposing that the alkali in soluble clay came from mica alone and that in the insoluble part, from feldspar,

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nor, even if this were the case, is there any reason for attributing to each portion a different function?"

It would first appear that he considered that alkali was there as a constituent part of feldspar, and then, later, that even though it may be present as a salt, it would make no difference for it is a product of the decomposition of feldspar. His reasoning here is fallacious.

His data shows that the bodies varied in constitution in more ways than merely in clay substance. He gives no evidence of this mineral constitution of the clays; hence, is presuming altogether too much in expecting his readers to take his word that the essential difference in the clay was in content of kaolinite. I maintain that he does not know and I ask him to state how he can know the mineral constitution of his clays. Ries touched upon this, and it certainly is in line with reason that since residual clays will contain whatever may result from the decomposition of the parent rock and that inasmuch as the parent rocks vary in mineral constitution, no two being alike, it is to be expected that the residual débris which we call kaolin *may be* largely composed of minerals other than kaolinite. Cook[1] as early as 1878 recognized this as did Johnson and Blake.[2]

Professor Binns speaks of the similarity of the coefficient of all the bodies as being worthy of note and takes this as seeming to show that clay substance, whether derived from kaolin or ball clay, acts in much the same manner.

By plotting these body formulae on the triaxial diagram, either those by weight, or the one he claims represents their mineral make-up, it at once becomes evident why the glazes crazed on all of them. They all fall well within the craze area. He has no argument for the value of the calculated rational analysis in this.

Nor is he justified in the conclusion that "the relative freedom of ball clays from crazing is probably due more

[1] Report on the Clay Deposits in New Jersey, 1878.
[2] Amer. Jour. Sci., 1867, p. 351.

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to their high content of quartz than to any radical difference in the clay substance," for he has neither shown that these clays differ in their quartz content nor that their influence in production of crazing is not due to a difference other than quartz content.

Professor Binns examined the clays with a high-power microscope and found that the kaolins are largely crystalline in character: "the kaolinite plates are distinctly visible and, in fact, form the bulk of the mass."

I can not credit the last clause of this quotation. I have elutriated kaolins, measuring the size of grains with the aid of a microscope and I have yet to find one kaolin in which kaolinitic grains form the bulk of the mass.

I have seen these flat plate-like grains in kaolins, but have never succeeded in proving that they were kaolinite grains rather than grains of mica. Merrill[1] does not check Professor Binns in his description of the Delaware kaolin, and Veatch[2] describes a microscopic examination of the Georgia kaolins as follows: "The clays were examined under the microscope, both in thin sections and as a powder unmounted. The clay substance appears, in the soft clays, in milky and translucent aggregates. *No kaolinite crystals were detected.* Quartz is present, usually as small angular and subangular particles, often coated with iron oxide. Angular, glassy, dark colored grains are frequently present and are probably smoky quartz."

In the first paragraph on page 203, Professor Binns states that the clay substance of clays are "identical in composition wherever it may be found" . . . . but . . . . "*it varies widely in constitution.*" I hold that this is not consistent with the implied synonymous use of the term clay substance and kaolinite (p. 200) and of the statement : "It will be seen that in this series of bodies there is only one variable, the *clay substance*, and that *this is varia-*

[1] See p. 297, "Rocks, Rock Weathering and Soils," for very instructive micrograms showing how unlike kaolinite grams are those found in kaolins.

[2] Geol. Surv. of Ga., p. 235, Bull. 18.

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ble only in physical form" (p. 202). Professor Binns is not consistent with himself.

His Method from a Practical Viewpoint: Even if Professor Binns was correct in all of his premises, observations and conclusions, I would still maintain that this analysis is useless and a dependence upon it full of risk to the potter. In making this claim, I am fully aware that I am throwing discredit on one of the profitable commercial opportunities of the consulting ceramic chemists of which I am one.

(1) If the formula which the potter aims to use for his body be plotted on the triaxial diagram, together with the weighings (in per cents.) which, according to either of these so-called rational methods of analysis, one is supposed to use the clays, feldspars and flint, it will be found that the desired formula is either nearer to or projected farther out into the area of the body compositions where, according to Hecht, the glaze will stand. In other words, by using these rational composition data, the potter would figure his composition to be safely within the "glaze fit area" and then weigh up his materials in proportions represented by points in the "craze area." I maintain that this is running a useless risk on the ultimate analysis being correctly made and especially so in view of the untenable assumptions on which the hypothetical constitution of the clay is based. I maintain that it is more logical to weigh safe and let the varying constitution of the clays project the real position of the body still further over into the glaze fit area.

(2) Then again there is a markedly close agreement in location of the boundary lines between crazing and glaze fit by Hecht and ourselves, although each were using different body materials. Hecht clearly shows the way these boundary lines would be shifted by using different proportions of ball and china clay. Would any one care to claim that these differences in location of the boundary lines are due wholly to differences in mineral makeup of the clays? If so, I challenge them to bring forward their

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proofs. I maintain that these differences in position of the boundary lines between glaze fit and craze areas are due more largely to physical differences in the clays than to chemical differences.

(3) Even though a chemical analysis was made showing that a clay was changing in its ultimate chemical composition, is there a potter who would know how that change was going to effect his body? I maintain that the mixture of an average sample from each new carload of clay with a given mixture of standard feldspar and flint, or of each new car load of feldspar with a standard mixture of clay and flint, etc., is the only rational and scientific way the potter has to test his materials. It is rational because it is to the point and is safe. It is scientific for it aims to do only the one thing that can be done rather than attempting such an impossibility as determining the mineral constitution of the materials.

Every potter should set aside at least one barrel each of china clay, ball clay, feldspar and flint, to mix with a sample of each new shipment of clay or feldspar according to an arbitrarily adopted formula. In this way he could readily detect all variations in the materials which would cause variations in his wares. This scheme would be far safer and much more rational than any chemical test ever devised.

I make claim, in closing, that the assumptions on which both of the so-called rational analyses are based, are not in agreement with facts; and further, that the results obtained do not justify the claims which have been made as reasons for adoption of these analyses by the clay worker.

Mr. Burt: Not to enter into a detail discussion, but merely considering the value of the rational analysis, in general, my opinion is that it is, at times, a valuable guide but is not to be depended upon as final in body composition. Suppose we have been using Florida or Georgia kaolin and now wish to use Missouri. Rational analysis may show that the Florida or Georgia carried less than 10 per cent. free silica while the Missouri has

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40 per cent. This I call valuable data that would help greatly in compounding a new mix. However, I agree entirely with Purdy that to determine the mineral constituents by rational analysis is impossible and while I am not quite prepared to say, as he does, that in glaze fit, physical differences are more important than chemical ones, I do believe they are equally important. One cannot work for any length of time with a range of bodies from the high flint white ware to pure clay terra cotta ones with no added flint without realizing that the mere chemical formula will not account for the glaze "fit" results obtained. I consider it foolish to even attempt to lay down any fixed rules, but generally speaking, my experience has shown that an open soft porous body is more liable to craze than a hard, partly fused, ringing body, whether it be white ware, tile, or terra cotta. I have elsewhere, offered a theory that much of the expansion of an open body is absorbed in its pore spaces and is not felt in the piece as a whole, hence, the less porous a body the greater as a whole will be its coefficient of expansion. Therefore, the physical property resulting from fusion becomes of prime importance.

We know that a frit fuses more readily, *i. e.*, at lower heat than its component parts mixed together but not previously fired. We also know that a mixture of the elements of kaolin will not give kaolin. Purdy cites Seger's work in analyzing Japanese porcelain, showing it could not be made from analysis. All of these lead me to agree with Purdy that rational analysis will not tell anything positively about the fusibility of the clay analyzed. Further, it fails to give any data in regard to fineness of grain which is also a very important factor in fusibility. So while I feel that the information given by rational analysis is valuable, a potter would not be warranted in assuming that a different clay giving same analysis would be the same.

As to the many vital characteristics of a clay, such as plasticity, softening with the water, shrinkage, color, and dry-

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ing properties, it, of course, tells us nothing. What information rational analysis does give is in no sense indispensable and does seem a lot of work for little return.

As I said, I do not agree with Purdy's statement that glaze fit depends more on physical than chemical difference. He would lead us to believe that, given a uniform physical condition, general uniformity would result. Assuredly, with coefficient of expansion, a physical phenomena as it is, then with same coefficient for glaze and body there would be a physical uniformity in this respect, but I do not believe that vitrification *per se* is more vital in determining this coefficient than is the question of whether you were vitrifying kaolin or pure silica. In other words, vitrification is important, but it is just as important to know what you are vitrifying.

On his assumption, we would say that any clay would fit a given glaze if fired to suitable physical condition. It is true each additional degree of heat changes the physical character of body or glaze so that undoubtedly a wide range is covered by any one mix, but no one mix has a wide enough range to cover all conditions. We have to widen and enlarge the field covered, varying our chemical composition just as we vary our heat treatment. It is possible that in bodies, the physical treatment is more important but in glazes I claim it is the chemical.

Now, Purdy charges the rational analysis with failing to determine the difference in mineral make-up of the clays. In this I agree with him, but he goes on to say he challenges any one to show that difference in mineral make-up makes any difference in glaze fit. In this, I do not agree with him. I fail to grasp Purdy's argument here. He seems to say that not the mineral make-up of the clay but its physical differences affect glaze fit. By this, does he mean there is no physical difference between different minerals? Certainly this cannot be. I claim that variation in mineral make-up of a clay means variation in physical and chemical characteristics and,

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mostly, to our sorrow, we potters know how great this variation is. What physical property is there in a clay except its coefficient of expansion that can determine a glaze fit? Greater or less porosity is a factor, coarse or fine grain, degree of weathering, method of manufacture into ware, degree of vitrification; all are important factors, but no more important than the chemical composition. Take porosity alone: if we were to say that because one clay fired to cone 5, absorbed 10 per cent. of water, gave a perfect glaze fit, hence, any clay that gave 10 per cent. absorb at cone 5, would fit same glaze, we would be wrong, one reason being that the two clays might be mineralogically entirely different.

It may be that Purdy does not mean clay in the broad sense generally accepted, but he does not qualify it.

As yet, no better theory has been offered to explain glaze "fit" (which new term I approve of and borrow from Purdy) than that of Seger, who claimed it was a question of uniform coefficient of body and glaze. I gather from Purdy's recent publications that he is aiming to show that we have in the past placed too much faith in this theory. He may be right and may prove his point, but in reaching this end, too much care cannot be spent in drawing general conclusions. This glaze fit problem that seems so simple is really, I believe, the result of a very complex group of factors and I should hesitate, to-day, to say that anything in the whole process was not a factor.

Mr. Purdy: What I had to say concerning the physical *vs.* chemical properties, and their effect on glaze fit, was meant to refer wholly to the clays used and not to body mixes:

Mr. Binns: The paper to which Mr. Purdy refers was written five years ago, not with the object of advocating the use of rational analysis but to criticize and discredit the laboratory method of digestion in sulphuric acid. I was not the first to use the calculation method. It was

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first set forth, so far as I know, by Buckley and Peppel, in the report on Wisconsin clays to which I referred.

Prof. Purdy states that "clay substance" and "kaolinite" are not the same thing. That is his opinion. I assumed that they are the same. I do not agree that the term "clay substance" should be referred to mere fineness of grain apart from composition. In the present state of our nomenclature it is not scientific to take a term used in one way by one group of men and assume that all others must use it in the same way. For example, Dr. Mellor, in his article on nomenclature of clays, "Transaction of English Ceramic Society," Vol. VII, proposes to use the term "clay substance" for everything that can be dissolved in strong sulphuric acid, thus including the carbonates and many minerals regardless of size of grain.

Prof. Purdy cites the case of Georgia clay which so far as the accepted definition goes is not a kaolin at all but a transported clay. I will go further than his challenge and state that as the term "kaolinite" has been used by me, both Georgia clay and Florida clay are 98 per cent. kaolinite, notwithstanding the fact that crystals cannot be found. Of course, my use of the terms may be wrong but at the time the paper was written the nomenclature had not been challenged.

My discussion of rational analysis has nothing to do with the composition or behavior of fire clays or stoneware clays. It refers entirely to the use of more or less pure clays in the potter's mix.

In his discussion of soluble alkali, Prof. Purdy entirely misses my point. I was referring, not to alkalies present as salts but to alkali appearing in the soluble part of a clay as shown by the laboratory method of rational analysis. My argument was that alkali had no legitimate place among the soluble constituents of a clay because its presence there merely showed that some of the feldspar in the clay had been decomposed and there was nothing to show that alkali calculated as a "soluble" ingredient would behave in a manner different from alkali reported

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as insoluble. This was, I think, first pointed out by Langenbeck in his "Chemistry of Pottery," and explained (as I think, erroneously) by the possible presence of mica.

So much for the "fallacious" reasoning. It is admitted on all sides, by myself included, that rational analysis rests upon certain assumptions. The term clay substance is referred to hydrous aluminum silicate, the product of decomposition, irrespective of the minerals and rocks from which it may have been derived. Of course there are differences in this substance, due largely to variations in size of grain, but my experience leads me to believe that these differences are not as great as Prof. Purdy states.

The feldspar, feldspathic matter or feldspathic detritus is likewise complicated in composition and structure but the assertion is, originated, I believe, by Seger, that in a pottery mix this mass acts, to all intents and purposes, as feldspar does. Hence, its amount may be derived directly from the alkali content of a clay.

In regard to the composition of my trial bodies no man in his senses would prescribe a body with 65 per cent. clay substance and expect a glaze to stand upon it. The bodies were intended to show crazing. The point was, not that they crazed but that the crazing was practically identical in size of mesh whatever clay was used. I have these trials by me still and the mesh of the crazing has not changed. In regard to the properties of ball clay, Prof. Purdy again misunderstands me. My point was that in the laboratory method of rational analysis, the proportions of the three assumed minerals, clay substance, feldspar and quartz, are so misplaced as to be misleading.

Seger spoke of ball clay as an efficient ingredient to arrest crazing, but he calculated his ball clays by the laboratory method, which made the quartz content appear higher than it really was. I calculated all the clays by the arithmetical method and found that the bodies made up held the glaze in the same way whatever clay was used. Prof. Purdy says that I have not shown that the clays used

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differ in their quartz content. On page 201, Vol. VIII, "Transactions A. S. C.," he will find the following:

	English ball clay	Florida clay	Tenn. ball No. 1	Delaware kaolin.	Georgia clay
Clay substance....	73.28	98.48	82.22	91.66	98.59
Feldspar.....	16.12	1.65	9.98	7.75	0.82
Quartz.....	10.00		8.55	1001	0.66

If this does not show that clays differ in their quartz content then I do not know the meaning of figures. Moreover, my point was especially that the ball clays carried a higher content of quartz than did the other clays, a fact which is also brought out by the laboratory method of rational analysis and even exaggerated.

In regard to the crystalline structure of the clays, certain illustrations have appeared since the work was done, *e. g.*, "English Transactions," Vol. VII, pp. 25–26, which show that I was mistaken. What I saw were the formations spoken of by Dr. Mellor in the same article as "curious aggregates of plate-like crystals," to which he refers the term "rouleaux" as suggested by Prof. Boyd Dawkins. Dr. Mellor further says: "We are not yet agreed as to the nature of these rouleaux." I believed them to be crystals but was apparently in error. They are certainly not grains of mica.

I fully admit that there are cases in which the adoption of calculation by rational analysis would make no change in the body as, for instance, where the amount of clay found in a sample of feldspar would offset the amount of feldspar found in a sample of clay but I have used feldspars with an alkali content of as low as 12 per cent. and as high as 15 per cent. Is it to be believed that one of these can be exchanged for the other, pound for pound, without effect? Or that a clay with 1 per cent. of feldspar in its composition can be exchanged for one with 10 per cent.? This is the only point upon which I would

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advocate the consideration of the rational composition of potter's materials. This, however, was not the main point of my paper.

In the year 1906, this position had not been seriously attacked and was, therefore, not defended. It is scarcely reasonable that Prof. Purdy should take the contribution referred to and attack it because it does not accomplish that for which it was never intended.

There is one more point. Prof. Purdy quotes Dr. Ries in a discussion of my paper and says it was a criticism of my assumed premises to which I have not replied, adding: "This should be done." The "assumed premises" were not mine but are as old as Seger and have been used by many writers. In fact, the statements made by Dr. Ries are not subversive of my argument in the least. They point out and emphasize facts to which every one will assent. I have admitted them all along.

Mr. Kerr: I cannot agree entirely with either Prof. Binns or Prof. Purdy on the question of rational analysis. My experience and study of the question have led me to believe that the rational analysis *is* of value, *within certain limitations* and that it is capable of improvement, but that, on the other hand, its wide application without regard to the limitations of its use would lead to disastrous results. The laboratory-made rational analysis is of value when applied to relatively pure materials and it can be successfully applied in comparing materials of the same general class. It cannot be applied promiscuously to materials differing widely in character, and in this criticism Prof. Binns seems to have all the argument on his side. Certainly where there exist such wide differences in the nature of the materials as existed between those used in making Japanese porcelain and those used by Seger in duplicating Japanese porcelain, the rational analysis is useless.

Concerning the "calculated rational analysis" there seems to be no real argument to support it while there are many arguments against it. A study of the formation of clays from the great varieties of parent rock should

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convince any one that a mineral analysis calculated from the ultimate composition must, in most cases, be very far from the truth. Equally convincing is the testimony offered by synthetic studies of mineral compositions in which the various constituents are derived from different mineralogical sources.

Prof. Purdy's suggestion, that clays should be tested by studying the vitrification behavior of samples made up with standard amounts of known feldspar and flint, is one that deserves adoption wherever it is not now in use. There is no other method so simple and at the present time we are not able to prescribe a more instructive test of wide application. But with some modifications which will be found to be necessary, the rational analysis or an entirely new method of mineral analysis (if that be necessary) should be made applicable to the study of raw materials. It seems very desirable that every encouragement should be given to the study of methods of making determinations of the kind, amount and physical condition of the mineral constituents of ceramic materials.

Do mica and feldspar have practically the same effect when present in a ceramic body? It has been proven that they do not, but since, in most of the raw materials, the amount of mica is relatively small, the error, due to classifying mica with feldspar, is usually unimportant. In the examination of materials that are highly micaceous the rational analysis is of practically no value.

Prof. Binns' statement that alkali has somewhat the same effect in whatever form it may be present is, so far as my experience goes, far from true. In general, the more satisfactory the material, the greater is the difference due to difference in the source of alkali. In fire clays the source of the alkali is of far more importance than the amount, perhaps for physical rather than chemical reasons. It is certainly not a safe assumption that in ceramic bodies the presence of a given amount of alkali may be taken as an indication of either the feldspar content or the vitrification behavior.

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In the application of *any* method of rational analysis, however perfectly it might be developed, it will always be necessary to consider the physical condition of the minerals present as well as their amounts. As much variation in the vitrification behavior of a body may be due to the physical condition as to the mineralogical source of any given constituent. A description of a ceramic material to be complete, therefore, should give not only the proportions of the constituent minerals but their physical properties as well. Both the methods and the interpretation of mineral analysis must be greatly improved before any such information can be obtained by its use.

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THE BEHAVIOR OF FIRE BRICKS UNDER LOAD CONDITIONS.[1]

By A. V. Bleininger and G. H. Brown.

In volume 12 of these Transactions the writers reported results obtained in testing full-sized fire bricks, under a load of 75 pounds per square inch at a temperature of 1300° C. In these tests, the bricks were placed on end, the load was kept constant and the heat was raised at a prescribed rate and maintained at the final temperature for a given length of time. The specimens were considered to have failed when they deformed badly, collapsed or broke or contracted more than one inch for the height of the standard fire brick.

A second series of tests was made with a somewhat higher temperature, 1350° C., but with a smaller load, 50 pounds per square inch. It is the purpose of this paper to report upon these tests and to coördinate them with last year's work.

From general considerations it is evident that as the temperature rises, the load carried must decrease within the range of the softening temperatures. Just where the lower limit of the softening is, depends, necessarily, upon the composition of the refractory. The more fluxing impurities the latter contains, the lower will be this point. For most refractory bodies it is not likely that this temperature is below 1150° C. Gary, in testing fire brick specimens, found that at 1000° C. no softening phenomena were noted. On the contrary, the crushing strengths of the fire brick cubes tested by him at this temperature were distinctly greater than that of the same materials at ordinary temperatures.

In comparing the results obtained in the two series of tests, 75 pounds at 1300° C., and 50 pounds at 1350°, respectively, it was found that the results were approxi-

[1] By permission of the Director of Bureau of Standards.

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mately the same, with the exception that the 1350°-50 pound tests appeared to be somewhat more sensitive and differentiated more sharply between the various kinds of refractories. This is shown by the fact that while a certain brand of brick failed in the lower temperature test by excessive contraction, it failed in the higher temperature test by collapsing. Also the compression effect in the second test was somewhat greater than in the first test. In one case the compression was greater in the 75 pounds than in the 50 pounds test. In this connection there must be remembered that the samples of brick were selected from stock and two bricks of the same brand do not necessarily possess the same composition.

Both tests, however, condemned inferior materials with practically equal certainty though the 1350° test, as has been said before, differentiated them more sharply.

In order to facilitate comparison, the results of both series of tests are given in this article. In Table I the chemical analyses are summarized, in Table II the empirical chemical formula, and in Table III the results of the physical tests.

It is observed that not all of the 1300° load tests were repeated but only a sufficient number to establish the relative severity of the tests. Such cases were selected in which a difference in behavior might be expected.

The specimens of sample No. 4 failed in both tests but the load of 75 pounds per square inch brought about more complete fracture. The result of the 1350°–50 pounds test on sample No. 4 is shown in Fig. 2. It is evident that the pressure effect is more dominant throughout the 1300°–75 pounds series while under the second conditions the softening, due to heat, is more pronounced. Figs. 3 and 4 represent two parallel tests, sample No. 12 having been subjected to the 1300°–75 pounds, and 12-B to the other test. Both conditions have brought about the same effect.

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Table I. Fire Brick Analyses.

No.	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	SO_3	H_2O at 100° C.	Ignition Loss	Total
1	81.60	14.55	1.15	0.49	0.37	0.27	0.67	1.08	..	..	..	100.18
2	79.20	17.42	1.19	0.49	0.21	0.38	0.37	0.91	..	..	..	100.17
3	77.02	18.35	1.32	0.52	0.48	0.28	0.67	1.49	..	..	..	100.13
4	54.58	37.35	4.10	1.57	0.54	0.53	0.42	1.02	..	..	..	100.11
5	54.70	39.72	1.32	1.86	0.29	0.52	0.64	1.07	..	..	..	100.12
6	54.69	38.86	1.41	1.92	0.35	0.52	0.91	1.57	..	..	..	100.23
7	54.25	38.90	1.83	1.92	0.41	0.78	0.78	1.26	..	..	..	100.13
8	52.30	41.52	1.28	2.46	1.02	0.45	0.28	0.94	..	..	..	100.25
9	63.89	29.28	2.05	2.40	0.27	0.29	0.40	1.71	..	..	..	100.29
10	60.37	34.83	1.37	2.05	0.39	0.31	0.20	0.67	..	..	..	100.19
11	61.35	32.65	2.15	1.98	0.46	0.50	0.17	0.86	..	..	..	100.12
12	55.66	36.52	2.59	2.40	0.49	0.61	0.18	1.73	..	..	..	100.18
13	68.73	25.12	2.26	1.32	0.36	0.49	0.25	1.62	..	..	..	100.15
14	60.77	32.63	2.89	1.94	1.12	0.26	0.26	0.46	..	..	..	100.33
15	56.55	36.64	2.84	1.90	1.34	0.22	0.32	0.43	..	..	..	100.25
16	50.76	44.24	1.45	2.03	0.33	0.29	0.34	0.60	..	..	..	100.04
17	62.14	32.29	2.65	1.42	0.71	0.50	0.13	0.38	..	..	..	100.22
18	62.74	31.80	2.45	1.53	0.75	0.56	0.18	0.18	..	..	..	100.19
19	35.46	57.98	1.40	2.70	0.29	0.29	0.75	1.30	..	..	..	100.17
20	52.89	43.41	0.90	2.12	0.16	0.13	0.36	0.27	..	..	..	100.24
21	65.41	29.50	2.75	1.38	0.45	0.25	0.10	0.34	..	..	..	100.18
22	66.53	28.66	2.35	1.36	0.58	0.42	0.28	0.19	..	..	..	100.37
23	66.28	29.12	1.55	1.79	0.59	0.23	0.27	0.30	..	..	..	100.13
24	77.82	19.00	1.01	1.65	0.22	0.06	0.10	0.28	..	..	..	100.14
25	56.62	39.19	1.95	1.69	0.36	0.08	0.18	0.19	..	..	..	100.26
26	54.51	40.42	1.90	2.46	0.35	0.17	0.16	0.20	..	..	..	100.17
27	65.59	28.95	1.45	0.93	0.35	0.60	0.63	1.21	..	..	0.45	100.16
28	62.81	31.85	1.27	1.33	0.28	tr.	0.53	1.72	tr.	0.05	0.30	100.14
29	68.15	26.30	1.97	1.10	0.11	0.23	0.56	1.53	..	..	0.25	100.20
30	65.34	30.01	1.45	0.88	0.18	0.52	0.38	1.21	..	..	0.28	100.25
31	72.74	17.77	0.80	1.55	0.13	tr.	0.13	0.27	..	0.18	6.55	100.12
32	56.69	29.48	1.20	1.87	0.25	0.12	0.36	1.21	tr.	0.82	8.20	100.20
33	53.27	31.72	1.16	1.93	0.21	0.08	0.30	0.97	tr.	0.83	9.72	100.19
34	66.05	25.45	1.06	1.40	0.20	0.37	0.30	1.05	tr.	0.23	4.05	100.16
35	58.88	26.41	1.35	1.22	0.35	0.42	0.34	1.64	0.01	0.72	8.85	100.19
36	64.70	21.90	1.47	0.86	0.45	0.60	0.42	2.16	0.02	0.65	6.96	100.19
37	85.00	10.55	2.85[1]	0.42	0.40	0.43	0.16	..	..	..	..	99.81
38	85.30	11.95	1.85[1]	0.30	0.20	0.29	0.24	..	..	..	..	100.13

[1] FeO.

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Table II. Chemical Formula.

No.	FeO	CaO	MgO	Na_2O	K_2O	
1	0.1006	0.0462	0.0473	0.0759	0.0805	0.3505 RO, 1.000 Al_2O_3, 9.534 SiO_2
2	0.0871	0.0218	0.0556	0.0348	0.0566	0.2559 RO, 1.000 Al_2O_3, 7.728 SiO_2
3	0.0917	0.0476	0.0389	0.0600	0.0881	0.3263 RO, 1.000 Al_2O_3, 7.135 SiO_2
4	0.1399	0.0263	0.0362	0.0184	0.0296	0.2504 RO, 1.000 Al_2O_3, 2.481 SiO_2
5	0.0423	0.0132	0.0333	0.0264	0.0292	0.1444 RO, 1.000 Al_2O_3, 2.341 SiO_2
6	0.0462	0.0164	0.0341	0.0385	0.0438	0.1790 RO, 1.000 Al_2O_3, 2.392 SiO_2
7	0.0599	0.0191	0.0511	0.0329	0.0351	0.1981 RO, 1.000 Al_2O_3, 2.371 SiO_2
8	0.0392	0.0447	0.0276	0.0110	0.0245	0.1470 RO, 1.000 Al_2O_3, 2.141 SiO_2
9	0.0895	0.0168	0.0253	0.0225	0.0636	0.2177 RO, 1.000 Al_2O_3, 3.722 SiO_2
10	0.0501	0.0203	0.0226	0.0094	0.0208	0.1232 RO, 1.000 Al_2O_3, 2.946 SiO_2
11	0.0839	0.0256	0.0390	0.0085	0.0286	0.1856 RO, 1.000 Al_2O_3, 3.194 SiO_2
12	0.0904	0.0244	0.0425	0.0081	0.0513	0.2167 RO, 1.000 Al_2O_3, 2.591 SiO_2
13	0.1147	0.0260	0.0497	0.0163	0.0699	0.2766 RO, 1.000 Al_2O_3, 4.651 SiO_2
14	0.1129	0.0625	0.0203	0.0130	0.0152	0.2239 RO, 1.000 Al_2O_3, 3.166 SiO_2
15	0.0988	0.0666	0.0153	0.0143	0.0127	0.2077 RO, 1.000 Al_2O_3, 2.623 SiO_2
16	0.0417	0.0136	0.0167	0.0126	0.0147	0.0993 RO, 1.000 Al_2O_3, 1.952 SiO_2
17	0.1046	0.0400	0.0394	0.0066	0.0127	0.2033 RO, 1.000 Al_2O_3, 3.271 SiO_2
18	0.0982	0.0429	0.0449	0.0093	0.0061	0.2014 RO, 10.00 Al_2O_3, 3.353 SiO_2
19	0.0307	0.0090	0.0127	0.0213	0.0243	0.0980 RO, 1.000 Al_2O_3, 1.039 SiO_2
20	0.0262	0.0066	0.0076	0.0136	0.0067	0.0607 RO, 1.000 Al_2O_3, 2.071 SiO_2
21	0.1188	0.0277	0.0216	0.0055	0.0124	0.1860 RO, 1.000 Al_2O_3, 3.769 SiO_2
22	0.1045	0.0368	0.0373	0.0161	0.0073	0.2019 RO, 1.000 Al_2O_3, 3.946 SiO_2
23	0.0678	0.0368	0.0201	0.0152	0.0111	0.1510 RO, 1.000 Al_2O_3, 3.869 SiO_2
24	0.0678	0.0210	0.0080	0.0086	0.0159	0.1213 RO, 1.000 Al_2O_3, 6.963 SiO_2
25	0.0634	0.0167	0.0052	0.0075	0.0052	0.0980 RO, 1.000 Al_2O_3, 2.456 SiO_2
26	0.0599	0.0157	0.0107	0.0065	0.0053	0.0981 RO, 1.000 Al_2O_3, 2.292 SiO_2
27	0.0638	0.0220	0.0528	0.0357	0.0453	0.2196 RO, 1.000 Al_2O_3, 3.851 SiO_2
28	0.0508	0.0160	....	0.0273	0.0585	0.1526 RO, 1.000 Al_2O_3, 3.352 SiO_2
29	0.0955	0.0076	0.0223	0.0350	0.0631	0.2235 RO, 1.000 Al_2O_3, 4.405 SiO_2
30	0.0616	0.0109	0.0441	0.0208	0.0437	0.1811 RO, 1.000 Al_2O_3, 3.701 SiO_2
31	0.0573	0.0133	....	0.0119	0.0164	0.0989 RO, 1.000 Al_2O_3, 6.959 SiO_2
32	0.0519	0.0154	0.0103	0.0200	0.0444	0.1420 RO, 1.000 Al_2O_3, 3.269 SiO_2
33	0.0466	0.0120	0.0064	0.0155	0.0331	0.1136 RO, 1.000 Al_2O_3, 2.854 SiO_2
34	0.0539	0.0142	0.0370	0.0193	0.0447	0.1691 RO, 1.000 Al_2O_3, 4.409 SiO_2
35	0.0655	0.0241	0.0405	0.0211	0.0673	0.2185 RO, 1.000 Al_2O_3, 3.783 SiO_2
36	0.0855	0.0374	0.0698	0.0315	0.1070	0.3312 RO, 1.000 Al_2O_3, 5.022 SiO_2
37	0.3826	0.0690	0.1039	0.0249	....	0.5804 RO, 1.000 Al_2O_3, 13.696 SiO_2
38	0.2107	0.0303	0.0618	0.0330	....	0.3358 RO, 1.000 Al_2O_3, 12.132 SiO_2

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Table III.

Results of Physical Tests.

No. 75–1300° C.

No.	Dimen's before	Dimen's after	Linear comp.	Deform. started	Cold crush strength	Per cent. por.
1	9″– 4 3/8″–2 1/2″	crushed	x	1213° C.	1464	30.2
2	9″– 4 3/8″–2 1/2″	crushed	x	1247	1289	30.1
3	8 7/8″–4 1/4″–2 1/2″	crushed	x	1210	989	32.4
4	9″– 4 1/2″–2 1/2″	crushed	x	1180	495	25.8
5	8 7/8″–4 1/4″–2 3/8″	8 1/8″–2 9/16″–4 1/2″	3/4″	1191	1160	23.0
6	9″– 2 3/8″–4 1/2″	8 1/4″–4 1/16″–2 7/16″	3/4″	1213	931	22.9
7	9″– 4 1/2″–2 1/2″	7 3/4″– 4 9/16″–2 5/8″	1 1/4″	1215	674	20.7
8	8 3/4″–4 1/4″–2 1/2″	8 3/8″– 2 5/8″– 4 1/4″	3/8″	1295	1082	17.1
9	8 7/8″–4 3/8″–2 3/8″	crushed	x	1191	612	29.4
10	8 7/8″–4 1/4″–2 1/2″	8 1/2″– 4 5/16″–2 1/2″	3/8″	1179	946	27.5
11	9″– 4 1/4″–2 1/2″	7 1/2″– 4 5/8″– 2 1/2″	1 1/2″	1133	480	25.1
12	9″– 2 1/2″–4 3/8″	crushed	x	1142	2614	24.5
13	8 3/4″–4 1/8″–2 1/2″	crushed	x	1130	843	22.5
14	8 7/8″–4 1/8″–2 1/2″	8 5/16″–4 1/4″– 2 7/16″	9/16″	1211	2226	25.5
15	8 7/8″–4 1/4″–2 1/4″	7 7/8″– 4 3/8″– 2 7/16″	1″	1234	1638	23.1
16	9″– 4 3/8″–2 1/2″	8″– 4 1/2″– 2 9/16″	1″	1205	971	24.3
17	8 3/4″–2 3/8″–4 1/4″	8 1/16″–4 3/8″– 2 1/2″	13/16″	1233	2578	23.9
18	8 7/8″–4 1/4″–2 1/2″	8 3/16″–4 9/16″–2 1/2″	13/16″	1274	955	21.0
19	9 1/8″–4 1/2″–2 1/2″	8 1/2″– 4 9/16″–2 1/2″	5/8″	1235	2071	33.3
20	8 3/4″–4 1/4″–2 1/2″	8 1/2″– 4 7/16″–2 1/2″	1/4″	1213	2005	26.8
21	8 7/8″–4 1/4″–2 1/2″	8 9/16″–4 3/8″– 2 7/16″	5/16″	1231	3174	22.2
22	8 7/8″–2 1/2″–4 1/4″	8 1/4″– 4 3/8″– 2 9/16″	5/16″	1234	2191	26.8
23	8 7/8″–4 3/8″–2 1/2″	8 5/16″–4 5/16″–2 1/2″	9/16″	1264	4234	23.9
24	9″– 2 1/2″–4 3/8″	8 7/8″– 2 1/2″– 4 3/8″	1/8″	0	2551	27.5
25	9″– 4 1/4″–2 3/8″	8 3/4″– 4 1/4″– 2 9/16″	1/4″	1291	1241	26.3
26	8 7/8″–4 1/4″–2 1/2″	7 5/8″– 4 1/2″– 2 1/2″	1 1/4″	1207	1138	22.3
27	8″– 2 1/4″–3 3/4″	crushed	x	1168	4042	18.1
28	9″– 4 1/2″–2 5/8″	8 5/8″– 4 1/2″– 2 5/8″	3/8″	1215	2509	27.4
29					4714	22.2
30					1585	27.9
31					1054	30.6
32					2829	3.25
33	No. 50–1300° Centigrade.				9008	12.4
34					7819	7.4
35	8 7/16″–4″– 2 1/8″	7 9/16″–4″– 2 1/8″	5/8″	1280° C.	7404	12.0
36	8 1/2″–4″– 2 1/4″	crushed	x	1200° C.	4368	17.4
37					1725	23.8
38					1910	23.8

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Table III—(*Continued*).

RESULTS OF PHYSICAL TESTS.

No. 75–1300° C.

No.	Dimen's before	Dimen's after	Linear comp.	Deform. started	Softening point in cones	Specific gravity
2-B	9′– $4^{3}/_{8}$″– $2^{3}/_{8}$″	crushed	x	1220° C.	28	2.671
					28	2.638
4-B	$8^{7}/_{8}$″– $4^{3}/_{8}$″– $2^{1}/_{2}$″	crushed	x	1175	28	2.635
					29	2.755
					$31^{1}/_{2}$	2.732
7-B	$8^{7}/_{8}$″– $4^{3}/_{8}$″– $2^{3}/_{8}$″	$8^{1}/_{8}$″–$4^{3}/_{8}$″–$2^{1}/_{2}$″	$^{3}/_{4}$″	1218	31	2.691
					31	2.717
9-B	9″– $2^{1}/_{2}$″–$4^{1}/_{4}$″	crushed	x	1238	34	2.712
					$29^{1}/_{2}$	2.674
11-B	$8^{7}/_{8}$″– $4^{3}/_{8}$″– $2^{3}/_{8}$″	crushed	x	1165	33	2.702
12-B	9″– $4^{3}/_{8}$″– $2^{3}/_{8}$″	crushed		1175	28	2.678
13-B	$8^{3}/_{4}$″– $4^{1}/_{4}$″– $2^{1}/_{2}$″	crushed		1150	$24^{1}/_{2}$	2.724
					$28^{1}/_{2}$	2.664
15-B	$8^{7}/_{8}$″– $4^{1}/_{4}$″– $2^{1}/_{2}$″	$7^{3}/_{4}$″–$4^{1}/_{2}$″–$2^{1}/_{2}$″	$1^{1}/_{8}$″	1245	$31^{1}/_{2}$	2.725
					31	2.705
					34	2.712
					31—	2.712
19-B	$9^{1}/_{16}$″–$4^{7}/_{16}$″–$2^{1}/_{16}$″	$8^{1}/_{2}$″–$4^{1}/_{2}$″–$2^{9}/_{16}$″	$^{9}/_{16}$″	1200	32	2.647
20-B	$8^{7}/_{8}$″– $2^{1}/_{2}$″– $4^{1}/_{4}$″				33+	2.975
					31	2.738
					31	2.668
					31	2.676
23-B	$8^{7}/_{8}$″– $2^{1}/_{2}$″– $4^{3}/_{8}$″	$8^{1}/_{8}$″–$4^{1}/_{2}$″–$2^{1}/_{2}$″	$^{3}/_{4}$″	1290	31	2.677
					29	2.622
					$31^{1}/_{2}$	2.702
26-B	9″– $4^{1}/_{4}$″–$2^{1}/_{2}$″	8″ $4^{3}/_{8}$″–$2^{1}/_{2}$″	1″	1220	31	2.744
					26	2.682
					$31^{1}/_{2}$	2.643
29	9″– $4^{1}/_{4}$″– $2^{1}/_{2}$″	crushed	x	1230	29	2.627
30	$8^{1}/_{2}$″– $4^{1}/_{4}$″– $2^{1}/_{4}$″	crushed	x	1180	$26^{1}/_{2}$	2.653
31	$8^{7}/_{8}$″– $4^{3}/_{8}$″– $2^{3}/_{8}$″	$8^{5}/_{8}$″–$4^{1}/_{2}$″–$2^{3}/_{8}$″	$^{1}/_{4}$″	1250	30	2.654
32	8″– $2^{1}/_{8}$″– $3^{3}/_{4}$″	$7^{1}/_{2}$″–$2^{1}/_{8}$″–$3^{7}/_{8}$″	$^{1}/_{2}$″	1330	31	2.565
33	$7^{7}/_{8}$″– $3^{3}/_{4}$″– 2″	$7^{3}/_{8}$″–$3^{3}/_{4}$″–2″	$^{1}/_{2}$″	1330	32	2.655
34	$8^{1}/_{4}$″– 4″– $2^{1}/_{4}$″	crushed	x	1180	25	2.524
35					$30^{1}/_{2}$	2.618
36					$27^{1}/_{2}$	2.649
37	$8^{3}/_{4}$″– $4^{1}/_{4}$″– $2^{1}/_{2}$″	crushed	x	1180	29	2.490
38	9″– $4^{1}/_{2}$″ { $3^{3}/_{4}$″ 2″	crushed	x	1150	29	2.575

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Further study of the behavior of fire bricks under load conditions has convinced the writers that this test not only is useful in testing refractories with reference to their load-carrying ability at furnace temperatures, but it seems to be an excellent means of getting at the real refractory value of a certain product. When we stop to consider furnace conditions it is at once evident that everywhere

Fig. 2.—Sample No. 4 tested at 1350° C., and under a load of 50 pounds per square inch.

pressures are to be resisted and not only those due to dead loads but also the compression and tension stresses caused by thermal contraction and expansion. As is seen from the results of these tests, the loads in question are not at all commensurate with the compression strengths of the product in the cold condition; in fact, are but a fraction of them. The higher the furnace temperature, the more rapidly is the load-carrying ability reduced until,

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finally, the refractory is unable to support its own weight. The load test, therefore, measures the viscosity of the fire brick at a certain temperature. Since any good refractory should possess enough rigidity at the temperature at which it is to be used to carry the load or to resist the pressure it is called upon to meet, it is evident that a fire brick, lacking in this respect, is as inferior as a material

Fig. 3.—Sample No. 12 tested at 1300° C., and under a load of 75 pounds per square inch.

showing a low softening temperature. As has been shown in the 1910 paper, an apparently high softening temperature is by no means coincident with high viscosity or load-resisting power.

There are yet to be met the questions as to whether the load test is fair to all kinds of refractories and what the conditions to be met should be. In the proposed test in which the temperature is 1350° C. and the load 50 pounds

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per square inch, it has been our purpose to suggest a test for high-grade clay refractories which would certainly reject any lower grade material. It has been successful in doing this, but whether it is too severe remains to be seen. In no case should a refractory be condemned entirely on the basis of this test. The softening temperature of a well selected sample or of several specimens (in the case

Fig. 4.—Sample tested at 1350° C., and under a load of 50 pounds per square inch.

of burnt bricks) should be determined and a chemical analysis should be made. The minimum softening temperature for a high-grade refractory should be cone 31. With reference to the chemical composition, it might be said that the RO content as calculated in the customary empirical formula should not exceed, in any case, 0.24

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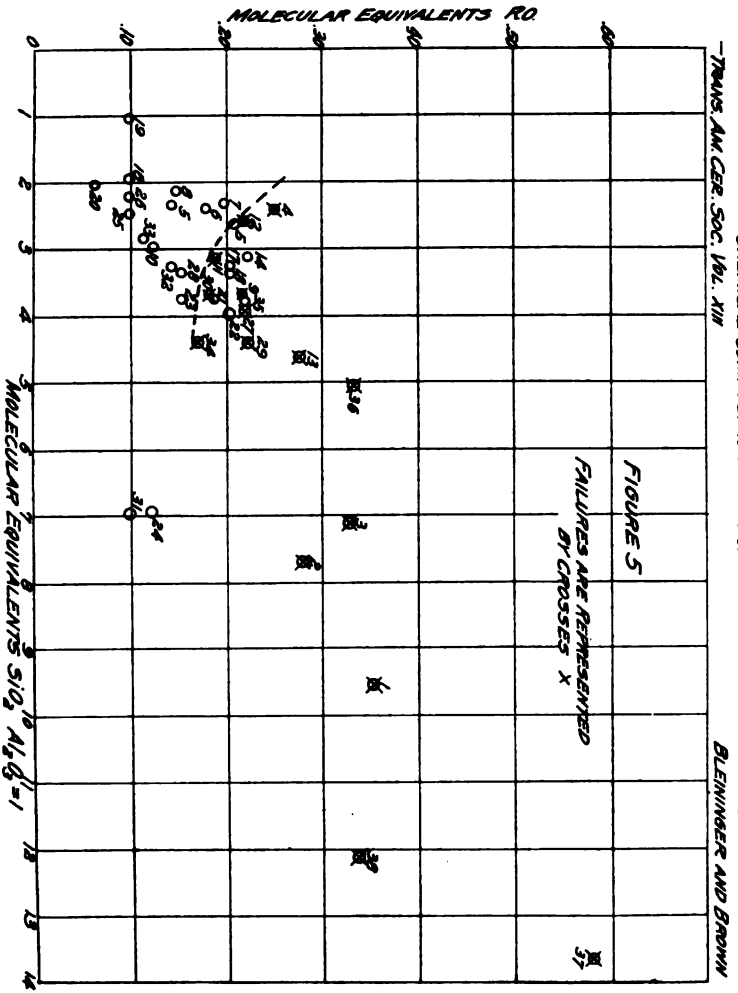
equivalent. In possession of these three data it is not a difficult matter to determine whether or not the refractory is a No. 1 material.



In Fig. 5, all of the tests made so far are incorporated in the chart showing the RO and SiO_2 content expressed in molecular equivalents. The alumina is, of course,

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equal to unity. It is observed that while failures occur even with as low as 0.17 equivalent RO this applies to a silicious material in which the fluxes appear to be more effective as has been pointed out by Richters in his tests of forty years ago. On the other hand, no materials appear to stand up which contain more than 0.225 equivalent RO. Owing to the fact that the chemical analyses made for this work under the direction of Mr. P. H. Bates, of the Pittsburg Laboratory of the Bureau of Standards, represent

Fig. 6.—Result of test of coke oven brick which had failed badly in actual use. Load applied based on mean cross section.

exceedingly careful work, this diagram represents relations of some importance.

Fig. 6 affords an illustration of a very inferior refractory failing utterly in its purpose. It represents a sample of wedge brick from a lot which proved to be very

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unsatisfactory in the coke ovens of the Jones and Laughlin Steel Co., of Pittsburg. In the 1350° load test the specimens failed long before the final temperature was reached.

It was thought advisable to make some tests involving changes in the shape of the test specimen. Thus, Fig. 7 shows a small pier built up of four half-bricks, representing a brand, No. 12, which had failed in the usual tests, as is shown in Figs. 3 and 4. The half-bricks were laid up solidly in good fire clay mortar and then subjected to the load of

Fig. 7.—Load test applied to a small pier consisting of bricks which had failed previously when tested on end.

50 pounds per square inch, at 1350°. The photograph (Fig. 7) shows that failure occurred very similarly to that observed in the previous tests of the same brand of bricks.

In order to illustrate the point brought out in the article of last year, as regards the improvement of the bond

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clay by adding to it some flint clay and grinding the mixture in a fine grinding machine like the ball mill, a clay of the No. 2 fire clay type was taken to represent an inferior bond clay. One set of auger machine bricks was made from the low-grade clay and another set from a mixture of 70 per cent. of this clay and 30 per cent. of high-grade flint clay, ground together in a ball mill to pass the 20-mesh sieve. Both kinds of bricks were burnt to cone 12 in a gas-fired test kiln.

Owing to the low refractory grade of the No. 2 fire

Fig. 8.—Brick made from plastic No. 2 fire clay tested at 1300° C., and under a load of 50 pounds per square inch.

clay, the conditions of the load test were modified in this special case by using the temperature of 1300° and keeping the load at 50 pounds per square inch. If this had not been done the specimen would have been distorted too badly

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for illustration purposes. The same test conditions were applied to the bricks made from the mixture.

In Fig. 8, the appearance of the brick made from the No. 2 fire clay is shown. It is seen to be hopelessly deficient in standing-up quality. The behavior of the bricks made from the finely ground flint-bond clay mixture is illustrated by Fig. 9. The improvement thus obtained is obvious and an example is thus afforded of how inferior bond clays

Fig. 9.—Brick made from a mixture of 70% No. 2 fire clay (sample No. 36) and 30% flint clay, tested at 1300° C., and under a load of 50 pounds per square inch.

may be improved by intimate grinding with some flint clay. By improving the quality of the bond clay, even though somewhat more of it may be used and adding the additional flint clay in the usual manner, it is evident that the refractory quality of the brick is decidedly improved.

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SUMMARY.

It is suggested that the load test under the conditions of a temperature of 1350° C. and a load of 50 pounds per square inch be used for the testing of high-grade refractories.

It has been found that no fire brick body showing a content of more than 0.225 equivalent RO was able to stand up under the above conditions and that with silica increasing above the $Al_2O_3 : 2SiO_2$ ratio the RO content becomes more effective in reducing the refractory value of the material. Thus, with 4.4 molecular equivalents of silica an RO content of 0.17 equivalent brought about failure in the load test.

The results obtained in previous work have been confirmed. Inferior bond clays have been shown to be improved by grinding intimately with flint clay.

DISCUSSION.

Mr. E. Gates: What pressure would you figure a good fire brick would stand at a temperature of 1300° C.?

Mr. Bleininger: We know that they should stand a pressure of 75 pounds per square inch at 1300° C. We have made experiments in which we used several pressures. With 125 pounds per square inch, most of the bricks failed. In fact, practically any fire brick will fail with that load.

Mr. E. Gates: What is the effect of size of grog?

Mr. Bleininger: We found that the denser and harder burned bricks stood best. None stood that had over 0.2 equivalent RO. Owing to the small load, a dense structure cannot be of primary importance, however.

Mr. Edgar: Did you find all plastic fire clays detrimental?

Mr. Bleininger: A plastic clay low in RO bases would not be detrimental. In most cases, however, the

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higher the content of flint fire clay, the more resistant were the bricks to deformation.

Mr. Barringer: Is there any relation between the crushing strength of the brick when cold and when heated at 1300° C.?

Mr. Bleininger: No.

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CUTLERY MARKS ON GLAZE.

By HARRISON EVERETT ASHLEY.[1]

One of the defects to which glazed tableware is subject is that of taking silver or black marks from the cutlery that is used with it. The English manufacturers appear to be more troubled by it than the American, the reason for which will appear as my paper proceeds. Several years ago they offered a prize to the pupils of the pottery school for a solution of the difficulty, but I have not heard of its being awarded to any one.

While making my comparative study of the effects of impure, brown boric acid and pure white boric acid in a white ware glaze (*Trans.*, **12**, 448), the ware was tested for crazing (*Trans.*, **9**, 59) by boiling for 8 hours in a saturated solution of common salt. The glaze made with pure boric acid came from the bath as bright as it left the kiln; but the brown acid glaze was sadly dulled—had lost its brilliant smoothness, and would take marks from pieces of metal drawn across it.

The explanation of this is that the sulphates remaining from the impurities of the brown acid were soluble in water, or became so affected by reacting chemically with the salt in the crazing test. This left cavities or roughness wherever they were dissolved out.

In domestic use and in the more exacting service of the quick lunch, besides the roughness from mechanical wear there is also the solvent effect of the somewhat salty dish-water which is slower in appearing than in my test because of lower temperature and greater dilution, but inevitable if the sulphates are in the glaze.

I have observed this to be more pronounced in ware of English manufacture than in the American ware with which I am most familiar. This I attribute to the exceedingly low sulphur content of the natural gas used by many

[1] By permission of the Director of the Bureau of Standards.

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American potters, as compared with the high sulphur content of the coal that the English potter is obliged to use. The advantage is partly sacrificed by the American if he uses the sulphur containing brown boric acid instead of the pure white boric acid.

As stated in my last year's paper, 100 parts of brown acid may be replaced by 70 parts white acid plus 15 parts borax, with decided advantage in all respects, and no disadvantages.

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CLAY AND KAOLIN MINING IN EUROPE.

By ARTHUR S. WATTS, Columbus, O.

The mining methods of Europe are, in many instances, far more primitive than those practiced in our own country, but whatever the method employed, the result is always the best product obtainable from the material at hand. No matter how great a saving can be effected by the use of some mechanical device, the labor-saver is unconditionally condemned, if the quality of the product is in any way endangered by its introduction.

Failure to appreciate the importance of this consideration is, to my mind, responsible for many of the failures in the exploitation of our American clays and kaolins. The universal complaint with American materials is lack of uniformity.

If our clay miners were confronted with half the difficulties that hamper some of our European cousins, I doubt if they would attempt to mine clay at all.

CLAY MINING OF SILESIA, EAST GERMANY.

In Silesia, East Germany, is an enormous area of useful clays varying from a very short but excellent fire clay to a very plastic potter's clay. At Siegersdorf, about 12 miles from Bunslau, are large workings of the average run of this clay which carries from 40 to 60 % of fine sand and a small content of alkali and lime, so that it forms alone a rather short open body. The illustrations (No. 474 and 475) show the method of working. The overburden consists of from 20′ to 40′ of sand with a small surface covering of loam. This is removed by the simplest pick and shovel method and loaded into cars and hauled from the working by a small locomotive. When the overburden is reduced to within a few feet of the top of the clay, the operation is suspended until the clay is about to be removed, thus preventing the exposure of the clay to contamination with foreign substances or the infiltration of iron bearing water.

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Plate 474.
Clay mining at Siegersdorf, Silesia, Germany.

Plate 475.
Clay pit near Siegersdorf, Silesia, Germany, about 12 miles from Bunzlau.

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The clay deposits are clean and uniform in quality throughout any given strata, although the various strata may differ considerably in composition and properties. Each stratum is carefully worked so that no mixing of different clays may occur. When a bench is broken down, the clay is sorted by women and any material from upper or lower benches which may be found is removed. These women also assist in loading it by hand into cars and it is hauled up an incline to the various drying sheds, or weathering platforms where it is stored until shipped. The clay here is suited for No. 2 fire brick and terra cotta, the best grade being used for cheap glazed wall tile, so much used in Europe.

In the immediate vicinity of these deposits and also to the south of Bunslau are beds of Fein Steinzeug Ton (fine stoneware clay). This clay is much fatter than the fire clay and, when washed free from sand, burns to a dense gray body at cone 10 to 12. As mined, however, it contains considerable coarse sand which must be removed if it is to be used for the better grades of pottery, but in its original state it furnishes a splendid material for the manufacture of stew-crocks and jars, and in the hundred of one-kiln pot-shops throughout this section, the horse-mill is the only clay-preparing apparatus employed. The mining of this clay is in keeping with the primitive methods employed in its working, since it consists of nothing more than a shaft sunk perpendicularly into the earth and surmounted by a simple hand-windlass for elevating the material to the surface (No. 476). The shaft is rarely more than 6 feet square and to ventilate the mine a wooden air flue is sunk in one corner, its mouth extending above the shed roof. The shaft is sunk with the greatest care and thoroughly cribbed from top to bottom. Between all cribbing and the face of the shaft, a layer of spruce or hemlock boughs is placed to insure against any overburden material sifting down into the workings.

The clay, which is found between two soft sand stones, is mined with pick and shovel, lifted to the surface in a hoist bucket, dumped into a car and removed to the weath-

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ering platform where it is spread in a layer from 2 to 2 1/2 feet deep to weather for a season. At the end of this time, its value can be determined by the amount of iron discoloration shown.

Some of these shafts are being worked where surface mining could be operated much more cheaply, but the rev-

Plate 476.

Fine stoneware clay mining near Bunzlau, Silesia, Germany.

enue from the clay is so small that property owners will not permit open mining, since it ruins the land for agriculture for many generations, while the shaft, on being abandoned, can be filled and leveled off and the land goes directly back to agriculture. This consideration is quite important since the land suited for agriculture in this section is limited.

CLAY MINING AT HALLE, SAXONY, GERMANY.

The most important kaolin center in Germany is Halle on the Saal River, where for more than a century, the kaolin for the Royal Berlin porcelain has been obtained. The kaolin here is mined by open pit, the deposit being a bed of sand carrying kaolin, and by sluice washing, as

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much sand as possible is removed. A peculiarity of this kaolin is the fact that it is so fat and its sand content is so fine grained that only a limited portion can be removed by sluicing, and wherever used it is always figured as a mixture of kaolin and flint.

KAOLIN MINING AT ZETTLITZ, BOHEMIA, AUSTRIA.

The highest grade kaolin mined in Europe, and probably in the world, is found at Zettlitz, a village in Bohemia, Austria, only about a mile distant from Carlsbad, the famous health resort.

The methods employed in mining are exceedingly crude, being in many cases the same as the shaft mining system in Silesia, and even in the most improved mines the equipment is only increased by the addition of a steam pump for draining the mine, and a steam hoist. Many years ago the mining of this kaolin was undertaken on an extensive scale, but the vein of water which feeds the "Grosse Sprudel" at Carlsbad was encountered, and only after a great deal of trouble and expense was the leak closed. The Austrian government realized the danger of permanently injuring this famous and valuable spring, and forbade open mining in future. With the shaft mining as operated at Zettlitz, of which No. 477 is a good example, only a limited amount of kaolin can be removed from one opening and, should a stream of water be encountered, the mine can quickly be filled and closed. The kaolin found here is mixed with three to four times its weight of sand and a small amount of muskovite, and, by a process of screening, the coarsest of these impurities is removed at the better operated mines. The large white pile in the right foreground of the picture consists of this refuse sand. The crude kaolin is then taken to commercial mills, where it is refined by means of settling tanks and the product is pressed in wooden filter presses and dried for shipping. The chief superiority of the Zettlitz kaolin over the Halle kaolin lies in the fact that the sand and mica in the Zettlitz material

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is coarse enough so that it can be removed by a settling process until less than 4% of sand remains.

Plate 477.
Typical kaolin mine from the Zettlitz district near Carlsbad, Bohemia.

KAOLIN MINING AT POMEISEL NEAR PILSEN, BOHEMIA.

In the neighborhood of Pomeisel, near Pilsen, is this same kaolin but slightly secondary and carrying 0.6 to 0.8% lime, while at Zettlitz it carries a maximum of 0.1%. The deposits at Pomeisel are nearer the surface than at Zettlitz, being covered in places by only a few feet of iron-bearing clay and sand. The mining here is all by open pits, as shown in No. 478, and operations are on a very extensive scale. The presence of modern engineering methods about these mines is very noticeable, but the same care noted in all operations in the smaller mines is also apparent. On removing the overburden, the top is stripped for a considerable distance, but a thin layer is left immediately over the kaolin to protect it from iron or dirt which might be washed in by rain. Vast banks of the finest clean sand from the settling tanks border the pits on all sides to keep out all surface drainage and dirt, and a thorough

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system of ditches drains all surface water away from the workings.

The deposit is 65 to 75% sand, and is loaded directly into wooden cars which are hauled by electrically driven cable out of the mine to the sifting house. Here the process of separating the kaolin from the sand and mica is carried on by means of a sand wheel, a mica settling tank

Plate 478.
Kaolin mines belonging to J. Elias & Co., Prag, Austria. Located at Podersam, about 60 miles due East from Carlsbad.

and fine-sand settling sluices followed by the final settling tank and filter presses. From the filter presses the clay goes to a drying house where warm air is forced by fans through the clay cakes and the mass is quickly dried. The entire process is carried on under roof and with every precaution to avoid dirt and dust reaching the kaolin either before or after its preparation.

KAOLIN MINING AT ST. YRIEIX, FRANCE.

St. Yrieix is the center of the kaolin-producing territory of France, and here is still being worked a treacherous

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vein of kaolin which appears and disappears along the face of a pegmatite vein. All French kaolin exists in these pocket-like deposits which demands that enormous quantities of refuse must be worked over in following the vein in the hope of finding a pocket of sufficient size to make mining profitable. Illustration No. 481 shows the present workings of the original kaolin mine at St. Yrieix, the pegmatite vein rising in the center of the picture while the soft and friable kaolin appears in the lower right-hand

Plate 481.

View of kaolin beds at St. Yrieix, France, about 25 miles south of Limoges.

corner and rises in benches almost to the head of the top of the pegmatite cliff. The methods of mining this kaolin are the crudest and most laborious I ever saw, but it goes without saying that the final product is a kaolin second to none in whiteness and purity. The process of winning this famous French kaolin is better observed at Montagnac, 3 miles east of St. Yrieix, where the workings are more modern but the process exactly the same. One of these mines I show you in picture No. 483, and another which better shows the enormous area covered in follow-

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ing this peculiar kaolin deposit is shown in No 484. In the former, the white kaolin is seen in the great nugget and also in the bank beyond. In the latter view the kaolin

Plate 483.
View of the kaolin mine at Montagnac, near St. Yrieix, France.

deposit is in the center of the workings and is noticeable from the clean benches exposed ready for removal to the sorting house which you see rising in the center background. The process of working is as follows:

When a trace of kaolin is found, a large pit is started,

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clearing the earth away from the center of operation and draining the surface water away from the workings. As soon as a pocket is found, all the loose material in that portion of the pit is cleared away and a cistern is sunk near the pocket to drain off all the water possible from the kaolin. The sand and granite refuse about the kaolin mass is cleared away from all sides so that it stands four or five feet above the floor of the pit. All is then made scrupulously clean and the work of removing the kaolin is

Plate 484.
View of a kaolin mine at Montagnac, near St. Yrieix, France.

begun. For this part of the work women and old men are employed entirely. With a tray about 20″ x 20″ x 5″ in size, they seat themselves about the kaolin mound and with a common steel table knife dig off chunks about the size of an egg until they have their tray full. This they carry on their head to the sorting shed where each piece is carefully cleaned of every particle of biotite, and also of any lumps of undecomposed granite present. The product is like meal and has been sorted during the process of cleaning so that three grades are produced—the pure white, the cream

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and the buff. The latter is about 50% of the total deposit and includes all kaolin that is stained from iron, and all of the material from the surfaces of the kaolin mass. Often in the center of a great block of white kaolin will be found a crevice filled with bright golden sand and kaolin. The hand-sorting enables this to be completely removed with little or no loss of high-grade kaolin. The kaolin can be washed free from the sand and mica, if desired, but this is seldom done, the different grades of kaolin being shipped with their sand content to Limoges or Sevres. For porcelain bodies, nothing is added except a small amount of feldspar, or flint, or both and the whole is ground together to the desired fineness.

The Limoges district is peculiar in that the manufacturers do not prepare their own bodies but buy them ready for the kneading machine and in some cases ready for the jigger. A porcelain body factory is a peculiar and interesting place. The stock consists of a dozen bins of various grade kaolins with their respective content of sand, and in addition to this a stock of pegmatite, flint and feldspar, all quite coarse. The grinding is all done in chaser mills made from barrels and to obtain a sufficiently fine sand requires about 24 hours.

PIPE CLAY MINING AT DEVONSHIRE, ENGLAND.

In England, the mining of clays is especially interesting. The mining of pipe-clays at Newton Abbot is shown in No. 471. This type of clay lies between the ball clay and the semi-plastic fire clay and resembles closely the plastic clay mined in Germany. All pipe clays are mined by open workings and the greatest care is exercised to keep the product free from foreign substances. The clay here shown is mined in two benches, the upper bench, however, being of an inferior grade and only the lower bench is mined by true pipe-clay mining methods. The digging is all by hand and the clay is taken out in shelves or tiers. A spade is used to cut the clay into uniform blocks about 9″ x 6″ x 6″ and these blocks are loaded by hand into a car

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in which they are brought to the surface and stacked on a wooden platform in regular tiers like brick. After a few days of air-drying the clay is shipped. Any blocks of clay that break or spall are called "Breaks" and are of a lower

Plate 471.

Pipe clay mines: Devon Clay Company, Newton Abbot, Devonshire, England.

grade than the solid blocks, owing to the higher sand content indicated. This clay is used for white smoking pipes, hence its name, and also more extensively for cheap white ware, yellow ware, and high-grade terra cotta.

BALL CLAY MINING AT DEVONSHIRE, ENGLAND.

Ball clay mining in Devon is a peculiar combination of pumping out water and mining clay. The ball clay and many of the pipe clay mines lie below the level of the river, and as the surface soil is a loose sand, the water filters in very rapidly and often two pumps are necessary to enable the clay miners to work. View No. 472 shows one of these pits being sunk, with the hoist on the left and the pumps in the rear. The cribbing necessary on account of the treacherous nature of the overburden is here shown.

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Ball clay is all shaft-mined. It lies in pockets near the pipe clay but generally at a lower level. The shaft is sunk to the bottom of the clay bed and the clay then taken out from all sides. The wet condition of the clay prevents it being cut into regular blocks, but it is handled in as large lumps as possible and sorted immediately on coming to the surface. View No. 473 shows a complete rig for

Plate 473.
Whiteway Bros.' ball and pipe clay mines, Newton Abbot, Devonshire, England.

mining ball clay, the hoist being shown swung back away from the shaft and the double pump in the foreground to the right. All the pumps in a district are driven from a central engine by means of the walking-beam system of power transmission, and pumping goes on night and day.

CHINA CLAY MINING AT CORNWALL, ENGLAND.

If the mining of ball clay in England is handicapped by the presence of water the mining of china clay is equally handicapped by the absence of clean water in sufficient quantity. Practically all the china clay of the Cornwall

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district is shipped from St. Austell. The china clay of England like the kaolins of France and Germany is mixed with many times its weight of quartz sand and other decomposition

Plate 468.
China clay mines of the Bloomdale China Clay Co., St. Austell, Cornwall, England.

products of granite, and often lies in enormous hills, side by side with vast deposits of undecomposed Cornwall stone. A stream of water is turned on the face of a cliff, as shown in view No. 468, and, by means of shovels and picks, the workmen cause the stream to spread itself about and float as much

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clay as possible. The clay-laden water rushes down the face of the hill through the sand and broken stone, the large particles of quartz and mica being practically certain of finding a lodging place along the way. At the foot of the steep descent, a long sloping bed of fine sand is encountered and through this the clay slip must work its way as shown in view No. 469, landing finally at the sluice level from which

Plate 469.
China clay mines of Bloomdale China Clay Co., St. Austell, Cornwall, England.
View at bottom of clay pit.

it is taken by trough to the pump which conveys it to the settling tanks above. The face of a clay mine from the top to sluice level is shown in view No. 470 in which the course of the water can be traced from the starting place in the upper center along the right side of the picture until it unites with other streams at the cistern in the lower right corner and is pumped to the sand and mica settling tanks on the hill 200 feet above.

In view No. 467 the clay-laden water enters the troughs in the center front and passes along these to the opposite end from which it passes to the circular tanks shown on

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the right, entering them at the bottom, and passing off at the opposite side top. By this time the clay is practically all settled and the water is returned clear for another bur-

Plate 470.
China clay mines of the Bloomdale China Clay Co., St. Austell, Cornwall, England.
General view of the hillside of kaolinitic material.

den of clay. The clay is allowed to accumulate in these tanks until it reaches the consistency of thick cream, when it is tapped off through a large main into the final settling

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Plate 467.

Clay refining plant of the Bloomdale China Clay Co., St. Austell, Cornwall, England.

Plate 466.

The final settling tank of the China clay refining process of the Bloomdale China Clay Co., St. Austell, Cornwall, England.

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tanks shown in view No. 466. These tanks are of concrete and the clay accumulates here and air dries until it can be handled with a hoe, when it is drawn into the tile-roofed house adjacent, which is equipped with long tile-covered drying kilns where the last of the water is removed by evaporation, and the china clay is ready for shipment.

DISCUSSION.

Mr. Barringer: Two things in this paper struck me very strongly: (1) The conservation of natural forces in Germany as an economic asset, carefully saving the top soil so that after the clay is removed there will still be a nice little farm; (2) the very careful preparation given to their clay.

Mr. Edgar: When speaking of the largest kaolin plant in Germany, you stated that they had a large content of sand which had to be washed out of the kaolin. I would like to know what method they used to remove the sand after it had been separated from the clay. I think you said they had from 40 to 60 per cent sand.

Mr. Watts: From the troughs it is hauled out into the bank in a wet state. A head of water is turned on in the troughs and the sand is washed out and down a hill. All those mines where they have kaolin washing, with the exception of Carlsbad, are gotten up as high as they can go and get water, so as to have plenty of room to get rid of their sand.

Mr. Edgar: In your last picture of the St. Austell mines you showed their process of settling out of the mica in mica sluices. Is that their only method of separating the mica from the clay?

Mr. Watts: That is the only way of getting it out. You know I mentioned that the clay has to go through a bed of coarse sand before it comes to the sluice where it is pumped up and I found on examination that there was very little mica left by the time it got to that final gate and cistern at the bottom. The material as it went into the mica trough was practically free from mica. I saw them rewashing refuse and asked: "Why do you go

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to all the bother of taking all this sand up the hill to wash it again? Why don't you agitate it down here?" They said they wanted to give it a chance to run down through the sand bed for the sand would catch practically all the mica before it got down to the cistern where they pumped it up on the hill.

Mr. Edgar: I understood filter presses were used in that district.

Mr. Watts: Filter presses are used.

Mr. Edgar: Do they leave it in that final settling tank for some time, unprotected from dirt contamination? Since they have a pumping station they must use considerable coal.

Mr. Watts: Yes, they undoubtedly do use some coal, but I did not see any evidence of dirt or refuse. They are very fussy about keeping their clay clean. For instance, a man never thinks of going into one of these houses without removing the shoes he is wearing, and putting on wooden shoes.

Mr. Sant: The clay must have been very much more difficult to reach over there than here. We have been somewhat reluctant to believe that the European clay miner has more difficulties to contend with than we have. Their natural advantages are certainly not any greater than ours, and their methods, compared with ours, seem to be more crude. I do not believe our men change their shoes when they go to lunch or anything of that sort, but we do exercise reasonable care to get out pure material.

Washing down the face of a kaolin bed to separate out the kaolin, as he described as being practiced in England, would be impractical in any deposit that I have seen in the United States, and even if it were practicable, it would seem that while the stream was washing down the kaolin, it would also wash down a good many other things we do not want. I would like to ask if this is not true in Europe?

I understand Mr. Watts to say that they get rid of their mica by settling. Mica does not settle, it floats. Mica in North Carolina occurs in small flakes and as long as

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there is any kaolin held in suspension, the slip will be heavy enough to float the mica. The only way we can get rid of mica is by sieving or by infiltration, and I do not believe the latter method has ever been tried here.

Mr. Watts: The amount of impurities washed down from the face of the English mines is very small, at least so far as I could observe. The material as it lays on the cliff is a mixture of sand, Cornwallstone, and mica, and every effort has been made to prevent surface material getting into the mine. The washing down of the whole face seems to remove the fine material, which is mostly kaolin. The amount of mica which reaches the settling tank, or the cistern at the foot of the incline after it has passed this comparatively level sand bed, is very small indeed so that when it enters the first of the mica sluices there is but little quantity of mica to remove. I saw them cleaning one of these flumes or sluices. The refuse they obtained was a kaolin-like material containing shining particles. I am inclined to think that the large area of sand was really their main filtering system.

Mr. Orton: In the kaolin mines at Dillsboro, North Carolina, the occurrence of the mineral is similar in nature to that of the St. Austell bed, excepting that the vein is very narrow compared to the enormous mass, which they seem to have at St. Austell. In the latter, they go down into a body of material of practically unlimited size, all of which is white burning. In the North Carolina proposition they are debarred from using the strake or water erosion process of mining because the vein is so narrow and surrounded with red burning materials on either side. In the kaolin mines in North Carolina which I visited, they were getting only 25 to 35 per cent. of kaolin, from 65 to 75 per cent. being coarse quartz, mica and various large-grained minerals. If water could have been allowed to run over the steeply inclined face of that material, it would have washed out the white, soft kaolinic material and left behind the coarse matter, but it would have also included the rusty and stained kaolin with the white.

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Mr. Edgar: I hardly agree that the foreigner has more obstacles to contend with than we have and I could not imagine a better proposition in mining than that in the English mines. They have no flumes to build and have water running over comparatively pure china clay. In North Carolina we had to run a pipe line for a long distance to get clear mountain water. There was water all around, but we were afraid of getting impurities from it. Then again the country was too rough to bring the clay to the railroad and we had to bring the clay as a slip three miles through a pipe line.

Florida clay contains from 60 to 80 per cent. of sand and the greater part of the clay is under water. Also the country is flat so that the removing of the sand, after it has been washed from the clay, is not always so easy a matter as it would be in a hilly country, such as those of Germany described by Mr. Watts.

When one considers the clay mining situation in the United States as a whole, as compared with that of Europe, I am inclined to think that the obstacles to be overcome in this country are greater than those of Europe, and that the American clay producers are not as well paid for their product and their efforts as are the European producers.

Mr. Sant: The proportion of mica in English, French and German kaolin must be very much smaller than it is in North Carolina, or quite generally in this country. Therefore, I think that that must be the reason they do not have any difficulty with it. In North Carolina mines, they will get a ton of scrap mica to ten tons of kaolin. They could not get rid of it by any system so far set forth. We cannot adopt other plans for various reasons, as for instance our labor conditions render the European method of working in this country impossible. They do not sift their clay, while every miner of china clay in this country, I believe, washes his clay through sieves, some of the mica being taken out in that way.

Mr. Speir: How many hours constitute a day's work for the women who carry the kaolin? How much

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are they paid per hour and how much clay do they carry in the course of a day's time in the trays on their heads?

Mr. Watts: I do not believe that the number of hours a person works gives a comprehensive idea unless you realize the amount of work they do. I do not believe that either one is worth considering unless you take into consideration the amount of pay that they get for a certain amount of work. In France these people possibly handle two tons of clay a day. They are paid from 20 to 25 cents a ton, that is, about 40 to 50 cents a day for cutting the clay out of the deposit and carrying it to the sorting house. The cleaning and sorting costs about 25 cents per ton of material handled, of which approximately one-half is marketable. After cleaning and sorting, the clay has to be hauled a very long distance by wagon to the railroad, which probably adds 60 to 70 cents a ton to the cost of the clay. In France they handle, conservatively speaking, probably one hundred tons of material for every ton of kaolin they get out. In Zettlitz, where labor is very much better paid, and the amount of material to be handled is not so great, they claim that the kaolin stands them about $12 a ton actual investment before they are ready to ship it, and we pay in the United States about $18 or $20 a ton for first-grade Zettlitz kaolin.

Mr. Speir: Then I understand these women make 40 to 50 cents a day and handle two tons a day in about eight or ten hours. I understand that there is considerable sand found in connection with this kaolin or clay. Has this sand any value in the state in which it is left after the clay is extracted from it, or could it by some inexpensive process be made to have value for the making of glass or pottery, or for use in the manufacture of silica brick, or for some other purpose? If not, why?

Mr. Watts: They have many thousand tons of sand with every little deposit of kaolin, and sand is a drug on the market. Mr. Elias said to me they would be glad to pay a man something to haul the sand off their property. This sand is used in the Bohemian Glass Works, but this really

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utilized but a trivial percentage of the amount available and the potteries require but little. In France the refuse from the kaolin cleaning is such an irregular mixture of pegmatite, biotite and quartz, that I doubt if it could be utilized in any ceramic manufacture.

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SOME EXPERIMENTS ON THE COLOR OF SODA-LIME GLASS.

By K. TAKAHASHI.

A glass made from sand, soda-ash and lime always has green tint due to presence of iron. To overcome this green tint and make the glass colorless, it is necessary to use a decolorizing agent. The most common decolorizer in practical use is pyrolusite, commonly called manganese.

Chemical Theory of Manganese as a Decolorizer.—In regard to the decolorizing action of manganese, there are two different theories: one chemical and the other physical. The chemical theory attributes this action to the oxidizing power of manganese dioxide. Ferric oxide imparts bluish green color to glass, and ferrous oxide gives yellowish green, which is less noticeable than the former. Manganese oxidizes ferrous oxide to ferric oxide, thus making the green tint less pronounced.

Physical Theory.—The physical theory explains this action by the chromatic action of pink from manganese on the green from the iron. Pink and green are complementary colors, and consequently manganese neutralizes greenish iron color and produces a colorless glass. Körner obtained a colorless glass from a mixture of red and violet glasses. Luckow obtained a colorless glass by melting copper oxide in a glass which was strongly tinted red by manganous oxide.

The writer thinks that the decolorizing action of manganese is mostly, if not altogether, due to its chromatic action. Under ordinary conditions, iron imparts bluish green color to the glass. The writer has failed to obtain yellow or yellowish green color from iron in soda-lime glass, even with a highly oxidizing batch. Glass containing manganese loses its pink color to some extent during annealing in a lehr, making it necessary to have the glass slightly pink before it goes into a lehr for otherwise, the glass would come out green. This fact also seems to

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show that the action of manganese is not chemical, because if it were chemical, it would not be necessary to have pink color before annealing, and it would not become green in the lehr.

The greatest trouble in making glass in a continuous tank containing 100 tons or more of glass is to keep a uniform color, and to get perfectly colorless glass day after day.

EXPERIMENTS TO DETERMINE INFLUENCE OF DIFFERENT MATERIALS ON COLOR.

The Base Batch.—The writer made some experiments to find the influence of different materials on the color of glass. The batches were melted in fire clay assay crucibles, in a down-draft test furnace. Natural gas was used as fuel, and air was supplied by means of a small blower. The following batch, except where otherwise stated, was used in all cases.

Sand.....	200 pounds
Soda ash.....	80 pounds
Burnt lime.....	23 pounds

When nitre was used, soda ash was reduced so that the soda content of the batch was the same.

The sand used for the experiments contains 99% SiO_2, and 0.06% Fe_2O_3. The soda ash is 58 per cent. ash, which contains about 99 per cent. of Na_2CO_3. The lime is high in magnesia, containing about 55 per cent. CaO, 38 per cent. MgO, and 0.1 per cent. Fe_2O_3.

A slight difference in conditions of the furnace or introduction of a little impurity had greater influence on the color of these small batches than they would on a larger batch in a larger furnace, hence, the writer does not claim that the result of these experiments are exactly comparable with those which would have been obtained in a tank furnace. It is very likely that on a larger scale more coloring matter would be required to produce the same color as

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was obtained in these small batches. It is reasonable to think, however, that if a certain batch gives a better color than others, that particular batch will likewise give a better color in a tank.

Manganese and Powder Blue.—Four series were compounded by adding the following proportions of manganese and powder blue to the base batch.

	No. 1	No. 2	No. 3	No. 4
Manganese	16 oz.	16 oz.	32 oz.	32 oz.
Powder blue	½ oz.	1 oz.	1 oz.	2 oz.

The powder blue used in the experiments analyzed as follows:

SiO_2	69.94
Fe_2O_3	0.17
Al_2O_3	0.92
Co_2O_3	5.29
Na_2O	0.41
K_2O	19.92
Loss on ignition	1.66

At 1320° C., No. 1 had greenish cast, and No. 2 had bluish shade. At 1425° C., No. 2 was bluish green, and its color was more pronounced than No. 1. A slight excess of blue is desirable as long as there is enough manganese to mask the iron color, but when manganese is "burnt out" and green color due to iron is brought out, blue intensifies the green tint and makes the color more pronounced.

With 32 ounces of manganese, one ounce powder blue gave dark red, even at 1425° C., while two ounces powder blue with 32 ounces of manganese gave only faint red at 1320° C., and purplish blue at 1425° C. From this, it is plain that the blue counteracts the coloring effect of manganese.

If we can regulate the amount of manganese to be used, so that there is just enough of it to neutralize the green color due to iron in the glass, there will be no necessity to use powder blue. But this condition cannot be attained

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in practice, especially in a continuous tank. To guard against fluctuation of purity of the raw materials, we use a little more manganese than necessary, and add a small amount of powder blue to mask pink color. Under ordinary conditions, 1/2 to 3/4 oz. of powder blue should be used.

Some glass makers adhere to certain ratio between manganese and powder blue, increasing powder blue with increase in manganese. But, from the above, it is apparent that you cannot set proportion of powder blue to manganese for all cases. It is true that under normal conditions, where manganese does not exceed 16 ounces, or thereabout, one part of powder blue to 16 parts manganese may be about right. But this does not apply when manganese is higher than 16 ounces. Increase of powder blue with increase of manganese is not only wasteful, but also injurious to the color, because excess of manganese and blue gives dark glass at best.

To study effect of powder blue on green glass in a tank, two batches were made, one with 20 ounces manganese, 1/2 ounce blue, and the other with 20 ounces manganese, one ounce blue. Green cullet was added to each in proportion of one part of cullet to one part of sand. Two batches showed little difference at low temperature, but at 1425° C., the one with one ounce of blue was decidedly darker green than the other.

Then, a batch with one ounce of blue and no manganese was made, and dark red cullet was added in the same proportion as in the former case. At low temperature, it gave light green, and as the temperature increased, the depth of green tint increased.

From the above results, it is seen that there is no use of increasing the blue when you want to overcome green. On the other hand, when you have "high color" in tank, an increase of blue will kill the red color.

White Oxide of Antimony.—A number of batches were made by adding 20 ounces manganese, 1/2 ounce powder blue, and white oxide of antimony in various quantities,

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from 2 ounces to 30 pounds per batch. The same batch with no antimony was also melted at the same time.

Without antimony, it gave decidedly green glass. Antimony in a small quantity gave good colorless glass. Two ounces of it gave as good if not better color as higher quantity of it. Above 10 pounds it gave a pale yellow color.

Needle Antimony.—A small amount of needle antimony had the same effect as white oxide of antimony, but a larger quantity of this substance produced greenish yellow color. Five pounds of it gave fairly dense color. This stronger coloring power of needle antimony over that of white oxide of antimony is possibly due to sulphur in needle antimony. Needle antimony is decomposed, setting sulphur free, which, when dissolved in glass, gives a yellow color thus augmenting the yellow color from antimony, giving a darker color.

Niter.—In order to determine influence of niter on color, especially when dirty cullet is uesd, three batches were made as follows:

	1	2	3
Sand	200 lbs.	200 lbs.	200 lbs.
Soda ash	80 "	78 "	76 "
Niter	0	3 "	6 "
Lime	23 "	23 "	23 "
Manganese	20 oz.	20 oz.	20 oz.
Powder blue	½ "	½ "	½ "

To each of these batches very dirty cullet was added in proportion of 1/2 part cullet to one part of sand.

No. 1, which contains no niter, gave decidedly green glass, and No. 2 and No. 3 were very much better, No. 2 being especially good.

Niter as an Oxidizing Agent.—Manganese in glass loses its color when it is reduced; therefore, it is objectionable to have a reducing agent in tank. The most common reducing agents, which we have in glass tanks, are smoky flame and organic matter, such as grease or dirt. For this reason,

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if we use dirty cullet, it requires more manganese to produce a colorless glass, and, also, it is harder to keep the color uniform because we do not know how much of reducing agent we are putting into the tank. Now, if we add niter, which is a strong oxidizing agent, it will counteract the reducing action, and keep manganese oxidized, causing the glass to hold its color with the use of less manganese.

FLUORSPAR.

To test influence of fluorspar, following batches were made:

	1 Pounds	2 Pounds	3 Pounds	4 Pounds	5 Pounds	6 Pounds	7 Pounds	8 Pounds
Sand.....	200	200	200	200	200	200	200	200
Soda.....	80	79	78	75	70	78	78	75
Lime.....	23	23	23	23	23	23	23	23
Fluorspar..	0	1	2	5	10	2	2	5
	Oz.	Oz.	Oz.	Oz.	Oz.	Oz.	Oz.	Oz.
White oxide of antimony..	0	0	0	0	0	2	5	2
Manganese...	20	16	20	20	20	20	20	20
Powder blue.	½	½	½	½	½	½	½	½

It was found that greater the amount of fluorspar used, better is the color. No. 7 and No. 8 were very good. Besides effecting the color, fluorspar makes the glass softer, and seems to make it easier to plain. If we can plain the glass in shorter time, we can pull the tank more. If the glass is worked out faster, it is subject to heat for a shorter time; consequently, less chance to burn out the color.

Feldspar.—Two to ten pounds of feldspar were tried, and it was found that with it the green color was increased. This is possibly due to the presence of a large amount of Al_2O_3, which seems to make the glass more susceptible to reducing action. The writer found a similar result in opal glass. Kaolin and free alumina have been tried as opacifiers,

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but they could not be used on account of bluish or greenish tint which they imparted to the glass.

Magnesia.—There is difference in opinion as to the influence of magnesia on the color. Some go so far as to assert that magnesia is necessary to obtain good colorless soda-lime glass. The writer made two batches, one with highly magnesium lime as before, and the other with very low magnesia, analysis of which is given below.

SiO_2	0.59
Fe_2O_3	0.05
Al_2O_3	0.28
CaO	96.84
MgO	0.72
Loss on ignition	1.40

Samples made from these two batches showed no difference in the color at all temperatures, but with low magnesia content, it required lower temperature and shorter time to plain the glass. This is beneficial for the same reason as explained in regard to fluorspar.

In conclusion, the writer wishes to acknowledge his indebtedness to the management of the Hazel-Atlas Glass Co. for granting permission to present this paper before the Society.

DISCUSSION.

Mr. Orton: Is your opinion about the alumina giving a greenish tint to the glass founded on experiments with pure oxide of alumina, or with aluminous minerals like feldspar and clay?

Mr. Takahashi: I tried feldspar and kaolin, and also calcined aluminum, and in all cases I got bluish or greenish tints.

Mr. Orton: Was the calcined alumina, that you added, the pure white material?

Mr. Takahashi: I got the material from a reliable firm, and although I did not make an analysis, I think it was quite pure.

Mr. Orton: The minerals containing oxide of alumi-

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num, especially the feldspars and kaolins, nearly always contain some iron, apparently in precipitated form. I have observed that whenever you add an aluminous mineral to a glass you get the green color. I have always believed that the iron carried in with the aluminous mineral was the cause of this effect.

Mr. Bleininger: I agree with Professor Orton that the color cannot be attributed to the alumina directly.

Mr. Takahashi: I do not think it is due to the presence of aluminum itself. Possibly it is due to some action of the alumina on some other element, or possibly the iron. I am not able to explain why it should exert that effect, but in my research I found a remarkable difference in tint with addition of very small amounts of alumina to a glass which contained none.

Mr. Purdy: J. Appert has discussed this point in an article to be found in the *Jour. Soc. Chem. Ind.*, **1896**, p. 357. He says: "One inconvenience, however, attends the introduction of alumina into colorless glass: namely, that it tends to give color, owing to its action on any iron oxide present."

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NOTES ON DR. H. HECHT'S INVESTIGATION OF SEVERAL RELATIONS BETWEEN PORCELAIN AND FELDSPATHIC EARTHENWARE.[1]

By HARRISON EVERETT ASHLEY.

Hecht's results are given in extensive tables, recording some 1,200 observations. It seems to me, however, much easier to comprehend them as a whole and also to study them in detail by means of diagrams. In place of copying his tables, I have prepared 14 diagrams, which contain the results of all these 1,200 observations on 75 different bodies.

The form of diagram chosen is the triaxial one, on which the location of a point tells its composition in clay substance, feldspar and silica. Contour lines are drawn through points having similar properties. For example, in Fig. 1, they are drawn through points that are at the limit, where good glazes cease and shivering begins.

In the equilateral triangle A B C (Fig.1), if any point F is taken, its distance from the three sides of the triangle will give the composition of the body it represents. The sum of the three distances is taken as always 100 per cent. The side AC represents 0 per cent. feldspar; the vertex B opposite represents 100 per cent. feldspar; F is 12.5 per cent. of the distance from AC to B and represents 12.5 per cent. feldspar. F is 30 per cent. of the distance from BC to A and represents 30 per cent. clay substance. F is 57.5 per cent. of the distance from AB to C and represents 57.5 per cent. silica. Similarly G represents 2.5 per cent. feldspar, 85 per cent. clay substance, and 12.5 per cent. silica. E is at 70 feldspar, 30 clay substance, zero silica. D is at zero feldspar, 30 clay substance, 70 silica. All possible combinations of the three substances are represented each by one point within the triangle.

With the clay substance from kaolin, Hecht found that with all compositions given by position in the Fig.

[1] Copied from Brick, Vol. XXIII. No. 3, by permission. Dr. H. Hecht's original article appeared in Thonindustrie-Zeitung (1897)

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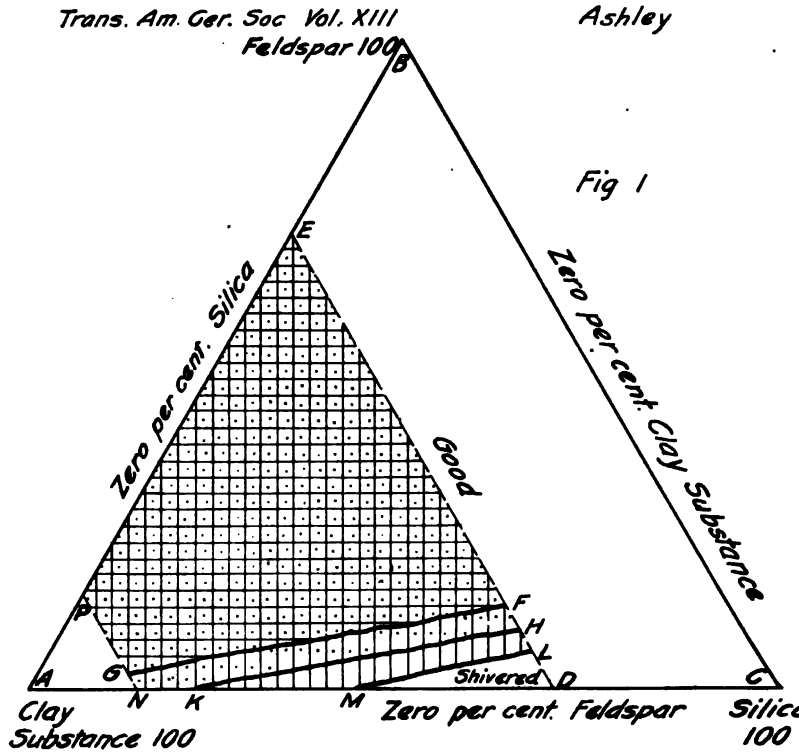

Description of Fig. 1.

Hard porcelain glaze $\left.\begin{matrix} 0.3\ K_2O \\ 0.7\ CaO \end{matrix}\right\} 1\ Al_2O_3\ 10SiO_2$.

Body and glaze burnt together at cone 16.

Horizontal hatching, region of good glazes when the clay substance is entirely from kaolin.

Vertical hatching, region of good glazes when the clay substance is entirely from plastic clay.

Dotted area, region of good glazes when the clay substance is half from kaolin, and half from plastic clay.

The regions with from 0 to 30 and 85 to 100 per cent. clay substance are untested.

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PE FG, the particular hard porcelain glaze held good, but with bodies of compositions given by G F D N, the glaze shivered. The regions A P G and E B C D were not tested. With half the clay substance from kaolin and half from plastic clay, the glaze held good in the region P E H K N, and shivered in the area K H D. With all the clay substance from plastic clay, good glazes were in the area P E L M N and shivered glazes in the area M L D.

Similar explanations hold for Figs. 2, 3, 4, 5, 6, 7 and 8.

The limits of translucency are shown by Fig. 9, and the limits of porosity by Fig. 10.

The per cent. of linear contraction for kaolin bodies at cones 09 and 10 is given in Figs. 11 and 12, and for plastic bodies in Figs. 13 and 14. Hecht says that, when half the clay substance is from plastic clay and half from kaolin, the shrinkage corresponds to the mean values of the tests on kaolin bodies and plastic bodies.

No tests of any kind were made on bodies with less than 30 per cent. clay substance or over 85 per cent.

The composition of the bodies is the same in clay substance, quartz and feldspar content, with the corresponding Arabic numeral. It passes through all gradations lying between the above-mentioned Wegeli body and the Copenhagen porcelain. Since at each point the clay substance consists once only of kaolin, once of half from kaolin and half from plastic clay, and finally is taken exclusively from a plastic clay, by this means there are given, with otherwise equal content in silicate of alumina, quartz and feldspar, the following noteworthy differences especially with regard to the holding of the glazes.

1. The Seger-porcelain glaze (Fig. 2), as well as the hard porcelain glaze (Fig. 1), holds more freely from crazing the higher the content of plastic clay is, as opposed to kaolin in the bodies. While the quartz-rich, non-feldspathic kaolin bodies, K 1, K 3, K 7 and K 11, are completely shattered by both glazes, a breaking-up does not take place with bodies made up of Westerwald clay with equal content of clay substance, quartz and feldspar.

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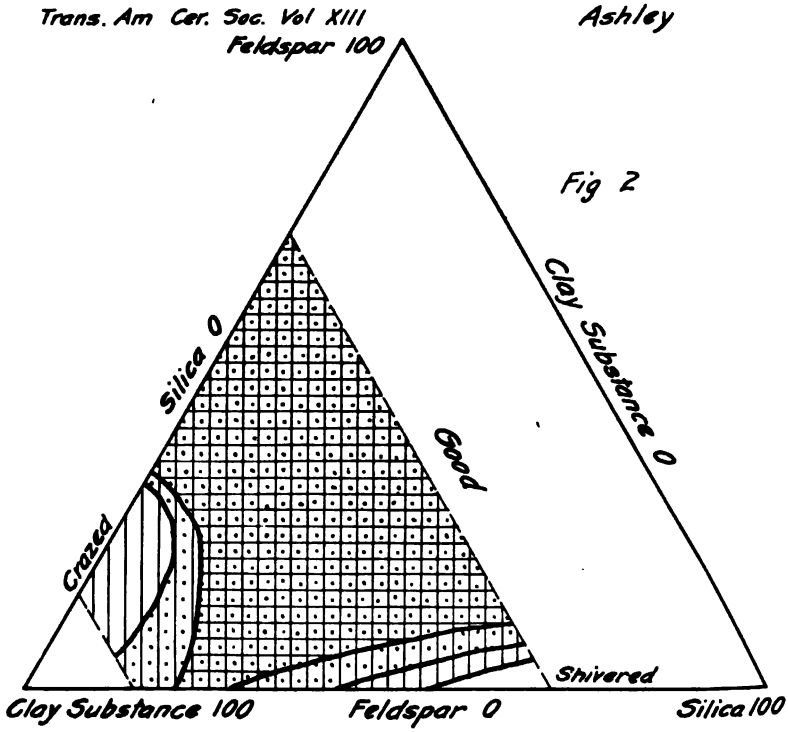

Description of Fig. 2.

Seger porcelain glaze $\left.\begin{matrix}0.3\ K_2O \\ 0.7\ CaO\end{matrix}\right\} 0.5Al_2O_3\ 4SiO_2$.

Body and glaze burnt together at cone 10.

Horizontal hatching, good glazes, kaolin clay substance.

Vertical hatching, good glazes, plastic clay substance.

Dotted area, good glazes, half kaolin, half plastic clay substance.

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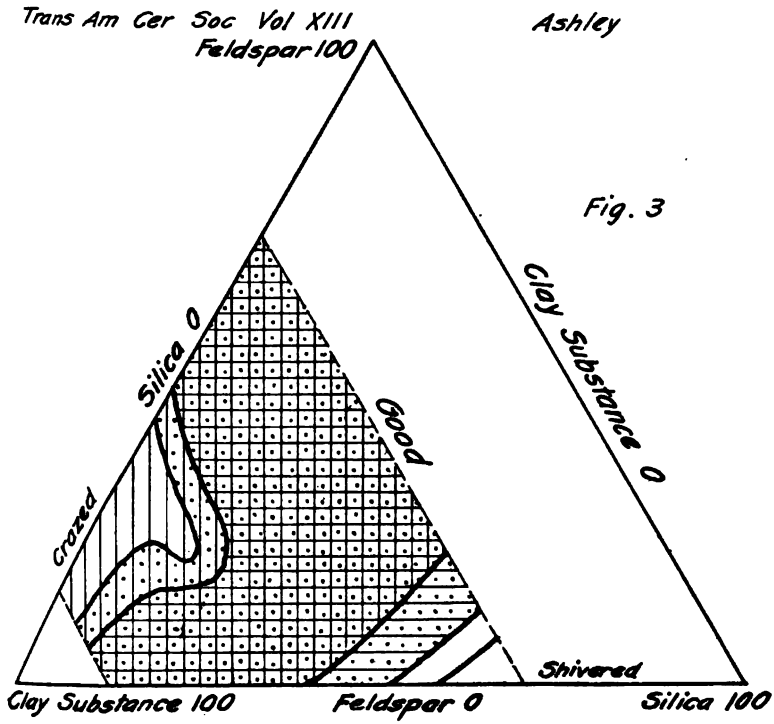

Description of Fig. 3.

Stoneware glaze No. 1 $\left.\begin{matrix}0.3\ K_2O\\0.7\ CaO\end{matrix}\right\}0.5\ Al_2O_3\left\{\begin{matrix}4.0\ SiO_2\\1.0\ B_2O_3\end{matrix}\right.$.

Biscuit fired at cone 6, glaze at cone 09.

Horizontal hatching, good glazes, kaolin clay substance.

Vertical hatching, good glazes, plastic clay substance.

Dotted area, half kaolin, half plastic clay substance.

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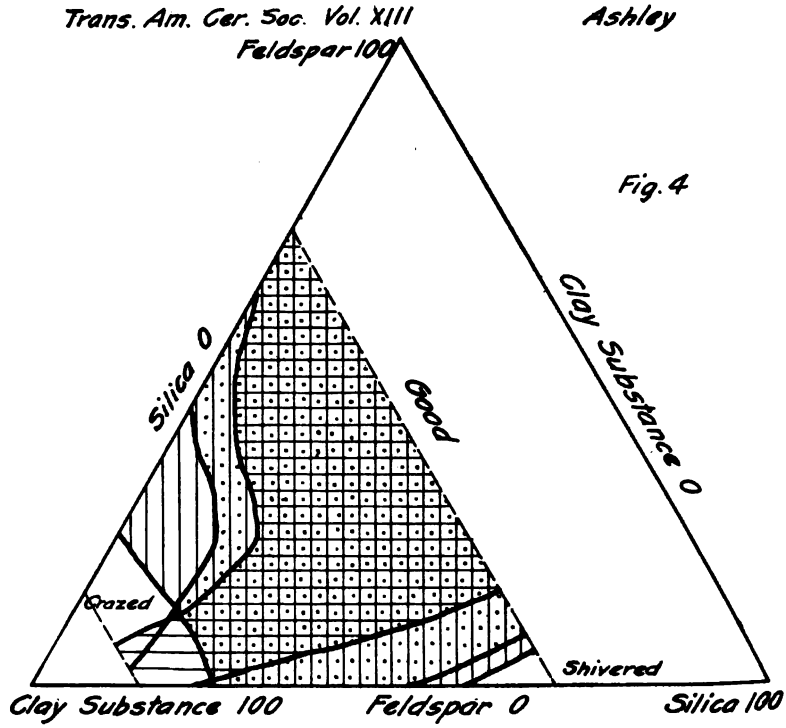

Description of Fig. 4.

Stoneware glaze No. 1 $\left.\begin{matrix}0.3\ K_2O\\0.7\ CaO\end{matrix}\right\}0.5\ Al_2O_3\left\{\begin{matrix}4.0\ SiO_2\\1.0\ B_2O_3\end{matrix}\right.$.

Biscuit fired at cone 10, glaze at cone 09.

Horizontal hatching, good glazes, kaolin clay substance.

Vertical hatching, good glazes, plastic clay substance.

Dotted area, good glazes, half kaolin, half plastic clay substance.

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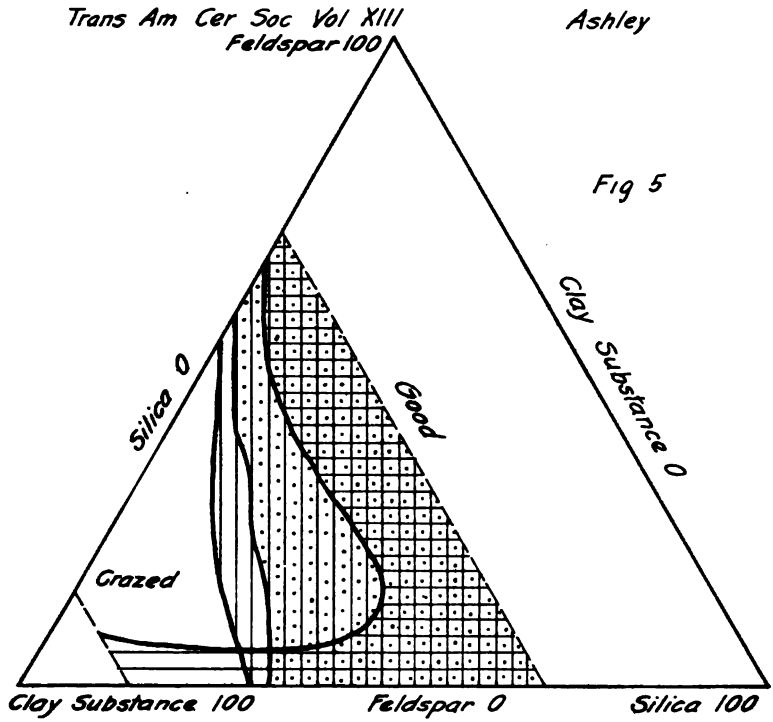

Description of Fig. 5.

Stoneware glaze No. 2 $\left.\begin{matrix}0.1\ K_2O \\ 0.3\ CaO \\ 0.6\ PbO\end{matrix}\right\}$ $0.2\ Al_2O_3 \left\{\begin{matrix}2.1\ SiO_2 \\ 0.4\ B_2O_3\end{matrix}\right.$.

Biscuit fired at cone 6, glaze at cone 09.

Horizontal hatching, good glazes, kaolin clay substance.

Vertical hatching, good glazes, plastic clay substance.

Dotted area, good glazes, half kaolin, half plastic clay substance.

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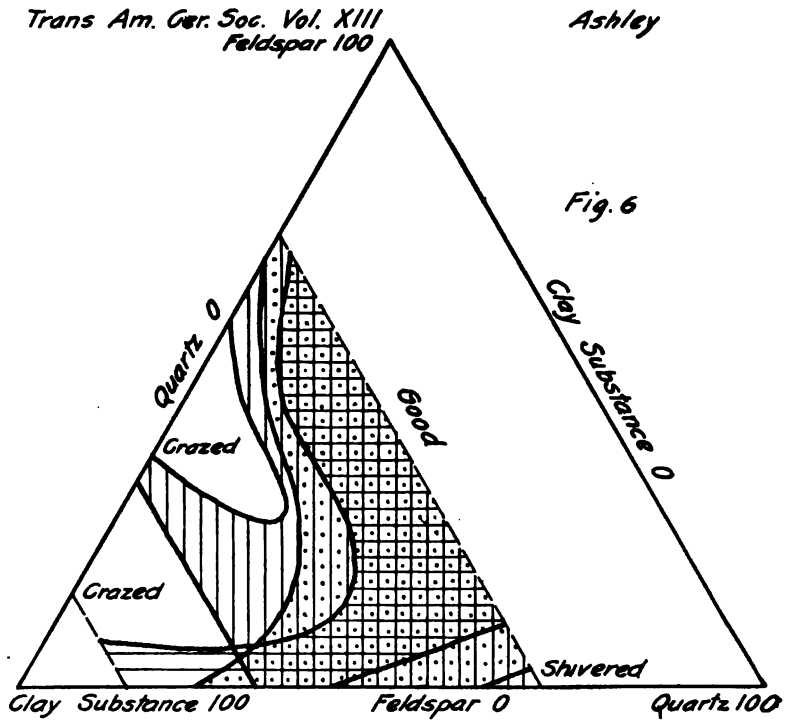

Description of Fig. 6.

Stoneware glaze No. 2 $\left.\begin{matrix}0.1\ K_2O\\0.3\ CaO\\0.6\ PbO\end{matrix}\right\}$ $0.2\ Al_2O_3 \begin{cases}2.1\ SiO_2\\0.4\ B_2O_3\end{cases}$.

Biscuit fired at cone 10, glaze at cone 09.

Horizontal hatching, good glazes, kaolin clay substance.

Vertical hatching, good glazes, plastic clay substance.

Dotted area, good glazes, half kaolin, half plastic clay substance.

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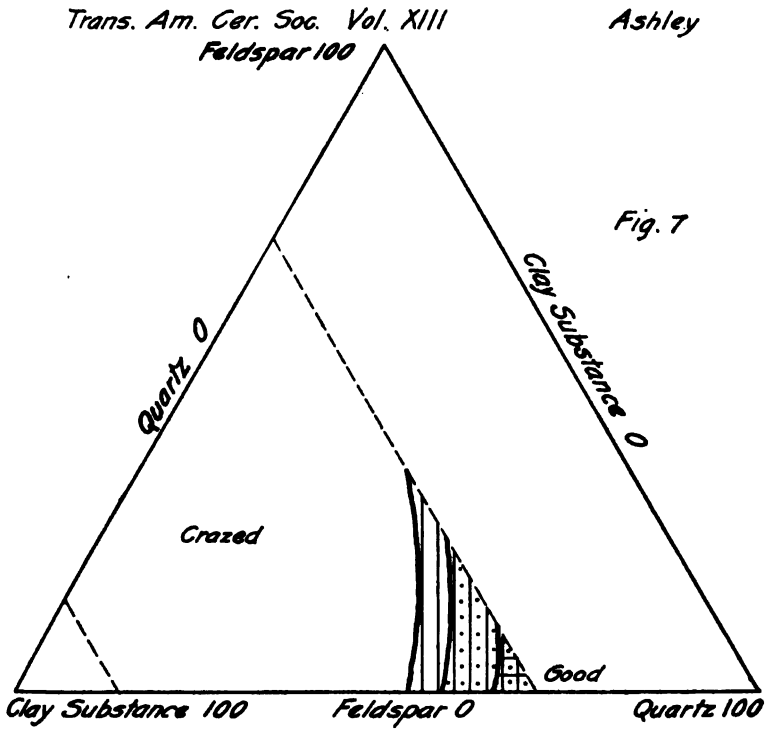

Description of Fig. 7.

Stoneware glaze No. 3 $\left.\begin{matrix} 0.25\ K_2O \\ 0.25\ Na_2O \\ 0.25\ CaO \\ 0.25\ BaO \end{matrix}\right\}$ $0.1\ Al_2O_3 \left\{\begin{matrix} 2.4\ SiO_2 \\ 0.6\ B_2O_3 \end{matrix}\right.$.

Biscuit fired at cone 6, glaze at cone 09.

Horizontal hatching, good glazes, kaolin clay substance.

Vertical hatching, good glazes, plastic clay substance.

Dotted area, good glazes, half kaolin, half plastic clay substance.

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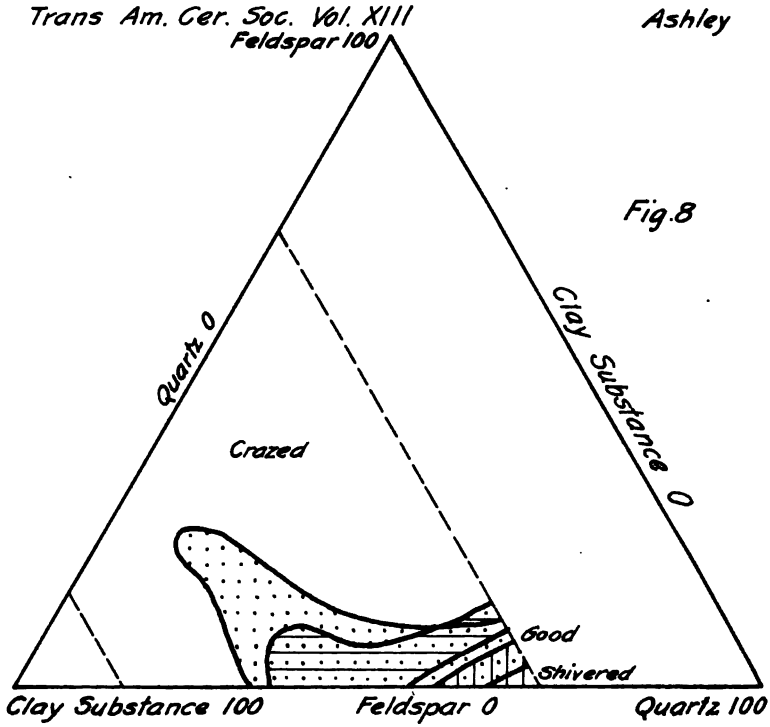

Description of Fig. 8.

Stoneware glaze No. 3 $\left.\begin{matrix} 0.25\ K_2O \\ 0.25\ Na_2O \\ 0.25\ CaO \\ 0.25\ BaO \end{matrix}\right\}$ $0.1\ Al_2O_3 \left\{\begin{matrix} 2.4\ SiO_2 \\ 0.6\ B_2O_3 \end{matrix}\right.$.

Biscuit fired at cone 10, glaze at cone 09.

Horizontal hatching, good glazes, kaolin clay substance.

Vertical hatching, good glazes, plastic clay substance.

Dotted area, good glaze, half kaolin, half plastic clay substance.

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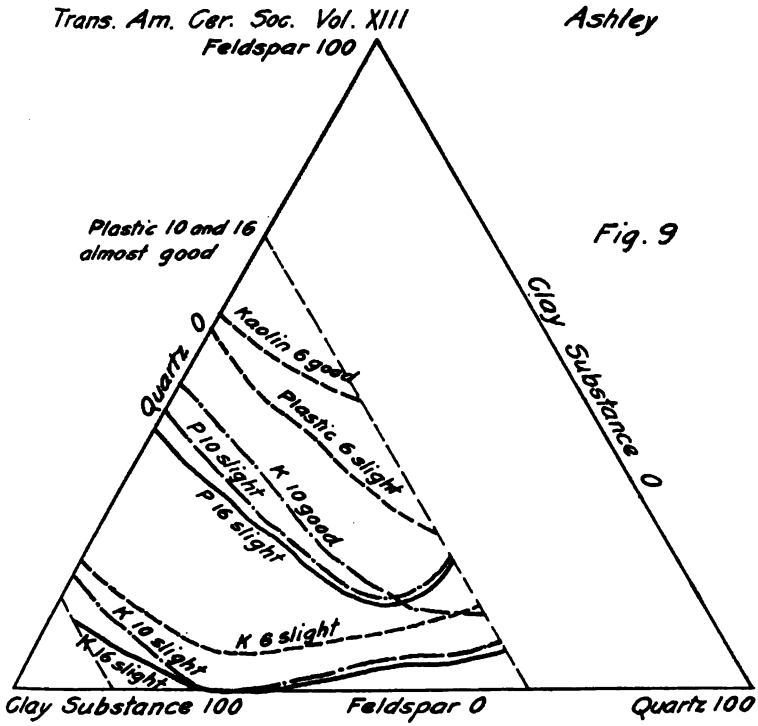

Description of Fig. 9.

Limits of translucency.

Results of cone 6 burn represented by dotted lines.

Results of cone 10 burn represented by dot and dash line.

Results of cone 16 burn represented by full line.

All trials become more translucent as the feldspar is raised and clay substance diminished. The limits shown are those at which the first slight translucency appears and those at which the translucency becomes good. When the clay substance is half from kaolin and half from plastic clay substance, the results are intermediate between those shown here.

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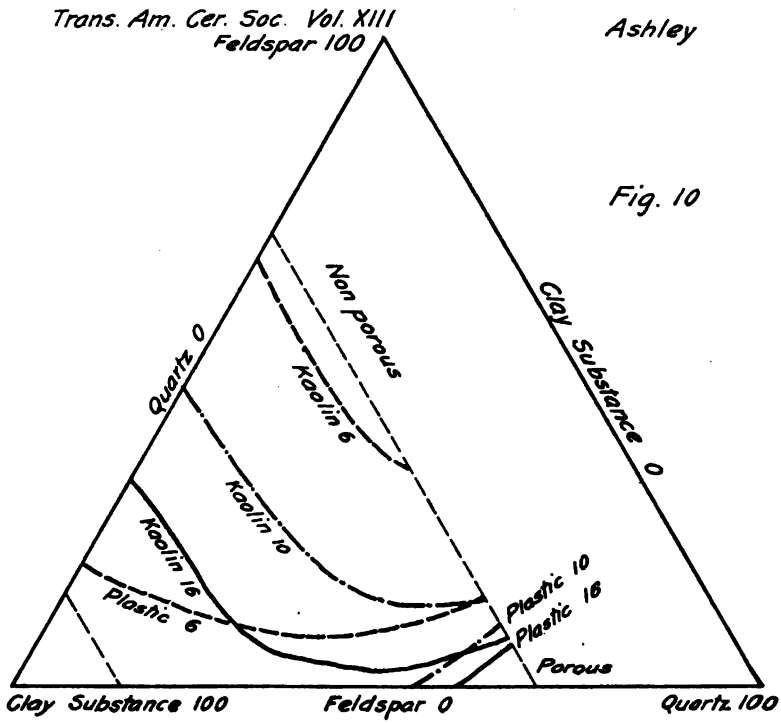

Description of Fig. 10.

Limit of porosity (character of the fracture).

Results of cone 6 burn represented by dotted lines.

Results of cone 10 burn represented by dot and dash lines.

Results of cone 16 burn represented by full line.

All of the trials lose their earthy fracture and cease to be porous as the feldspar increases and the clay substance diminishes. The contour lines show where the porosity ceases. When the clay substance is half from kaolin and half from plastic clay, the results are intermediate between those shown here.

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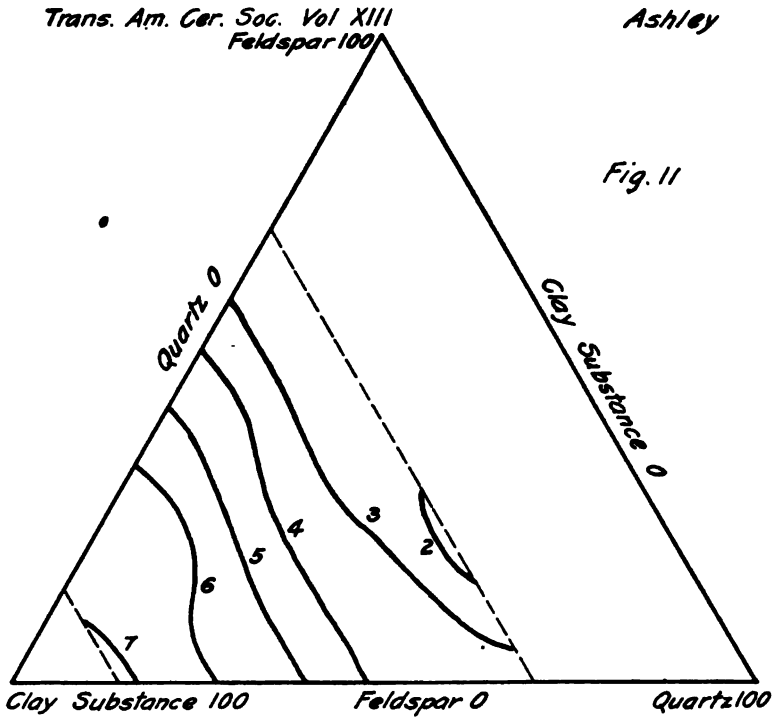

Description of Fig. 11.

Per cent. of linear contraction.

Bodies containing clay substance from kaolin, fired at cone 09.

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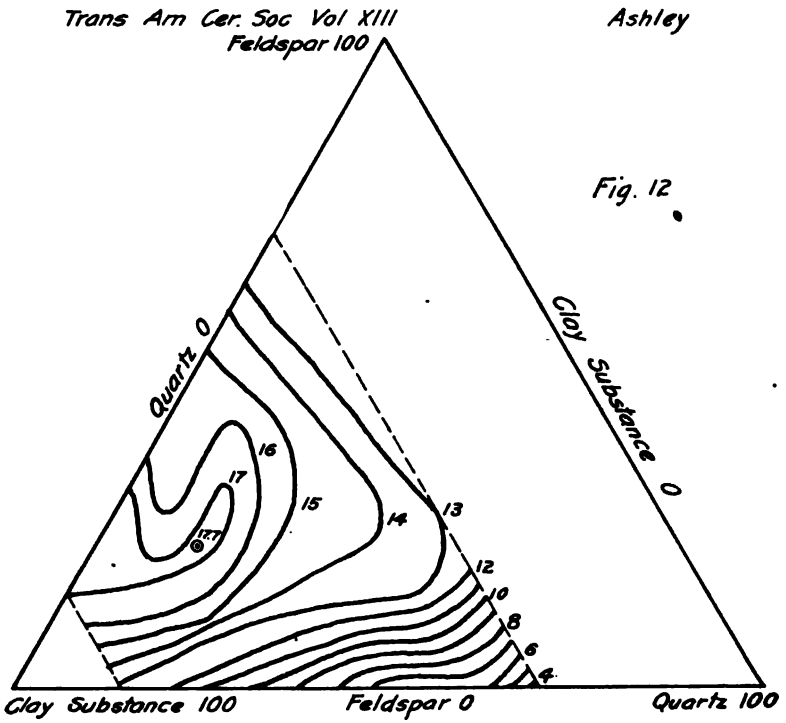

Description of Fig. 12.

Per cent. of linear contraction.
Bodies containing clay substance from kaolin, fired at cone 10.

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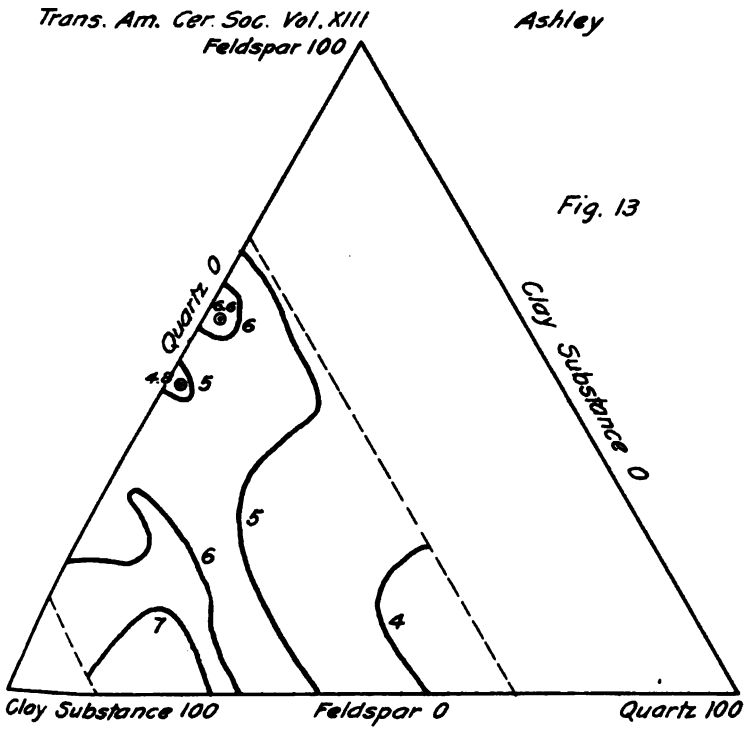

Description of Fig. 13.

Per cent. of linear contraction.

Bodies containing clay substance from plastic clay, fired at cone 09.

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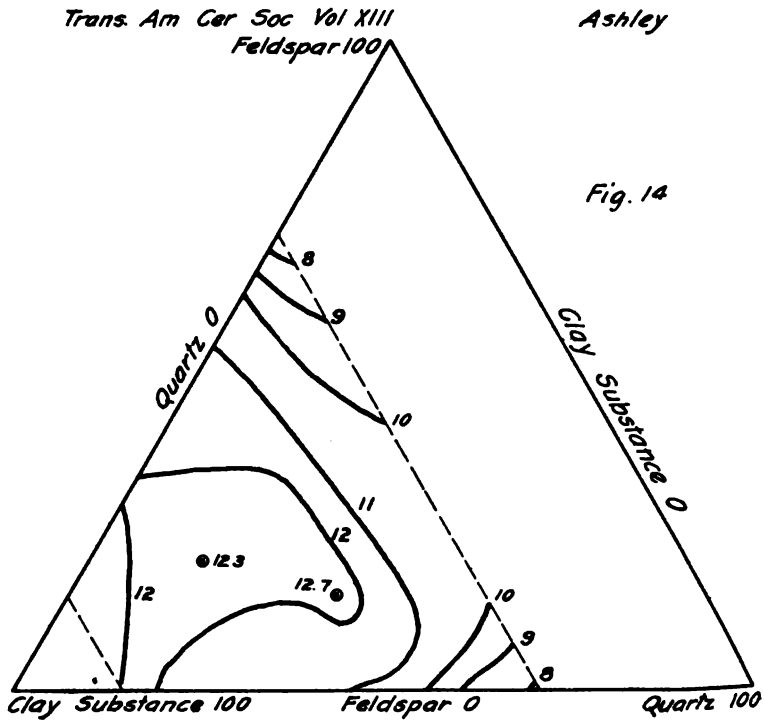

Description of Fig. 14.

Per cent. of linear contraction.

Bodies containing clay substance from plastic clay, fired at cone 10.

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Earthenware glaze No. 1 (Figs. 3 and 4) behaves similarly to the two series. It still holds, however, upon the kaolin bodies if the biscuit burn of the ware was not too high.

2. With the feldspathic bodies, the porcelain glaze and the earthenware glaze hold free from crazing so much the earlier, the higher the quartz content. They tend, however, to become crazed with a decreased quartz content. The earthenware glazes 2 and 3 (Figs. 5, 6, 7 and 8) show exactly the opposite relations, in that their ability to hold upon the new feldspathic bodies increases with increasing quartz content. With these again, the plastic clay acts more favorably upon the holding power of the glazes than the kaolin, and the lead glaze is earlier free from crazing than the leadless baryta glaze.

3. If the quartz in the bodies is step by step replaced by feldspar, the porcelain glazes become able to hold on the kaolin bodies; this is much more apparent with the increase of quartz and feldspar content or with the decrease of clay substance content. Upon the clay bodies, both the glazes hold also, even with high content in clay substance. Earthenware glaze No. 1 behaves similarly when the biscuit burn of the ware has not been too high.

The lead-free barium glaze behaves altogether differently. Upon the kaolin bodies it shows, on the whole, only small tendency to hold; only the bodies K 7 and K 11, indeed, show themselves free from defects in holding. On the other hand, it is able to hold on non-feldspathic clay bodies when the quartz content is large enough.

4. With regard to the translucency (Fig. 9) and the character of the fracture (Fig. 10), it appears from the tables (here substituted by diagrams) that many a product will always give a porcelain with sufficiently high burning, while at lower firing it may be claimed only as earthenware. Translucency occurs with kaolin bodies much earlier than with clay bodies; in addition, they burn in the reducing flame throughout to a white color tone and, while in the oxidizing flame, to an ivory-like yellowish tone.

In regard to the composition of the bodies, there is

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established by this investigation that the feldspathic soft porcelains, upon raising the content of clay substance at the expense of the content of feldspar, go over to earthenware; also that earthenware high content in clay substance differs from the difficultly fusible porcelain only in that the latter are burnt at higher temperatures. Feldspathic earthenware, poor in lime, rich in clay substance, forms, therefore, the intermediate stage between soft and hard porcelains. Through careful selection, either of a slightly plastic kaolin or of an exceedingly plastic clay, there can generally be found a product which (partly in consequence of the heat given) is so variable in its properties that it may be called either porcelain or earthenware. Its classification will be determined by its behavior to the specific glazes, according to whether the ware is vitreous or earthy and porous.

For earthenware, porcelain glazes of stable quality can be produced which are especially suitable for household utensils made from slightly-shrinking and heat-resisting bodies. The value of these wares is increased according to their resistance to acids, alkalies and fats, and this is attained by the burning on of a hard porcelain glaze, which is more resistant to their attack than is an easily fusible glaze.

Moreover, by proving, on the other hand, that easily fusible glazes hold without crazing upon the most different bodies, even when they are burnt to the density and translucency of porcelain (and therefore are to be taken as porcelain), there is considerably increased the ability to decorate porcelain wit hunderglaze designs and with colored glaze. Thus, for porcelain, which has the advantage of transparency over earthenware, there is gained the same artistic range in regard to decorative painting.

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THE COMMERCIAL CLAYS OF UTAH.

By A. F. GREAVES-WALKER.

The state of Utah is remarkable from a clayworker's standpoint, principally from the fact that it has so few clays of any commercial value.

True, there is plenty of clay such as it is, as would be natural in a country where every valley has been a lake bed in recent geological times. But most of these old lake bed clays are of no value because they contain various and generally large quantities of the alkalies and alkaline earths. Sometimes these salts run so high that the material would be more valuable to a salt refiner than a clayworker. However, the best of these lake bed clays, together with those which have been deposited at the mouths of the canyons very recently, are used to some extent for common, and in some cases for pressed brick manufacture.

These clays are almost identical in composition with the glacial clays of the North and Northeast. They always contain a high percentage of lime, iron and alkali, the lime predominating and sometimes running as high as 30 per cent. $CaCO_3$.

As is usually the case with this class of clays, the upper few feet has been weathered to such an extent that it burns to a red color. From this surface clay all of the red pressed brick made in the state are manufactured. It is of such poor quality, however, that the brick must be soft burned, and as a consequence the high alkali content causes them to scum as soon as they are placed in the wall.

Beneath this surface clay the main body of yellow burning clay is found. From this material all of the common wire cut and yellow pressed brick are made.

Both kinds of clay produce very poor brick, but the scarcity or inaccessibility of anything better makes it necessary to use them.

It might naturally be expected that with so many

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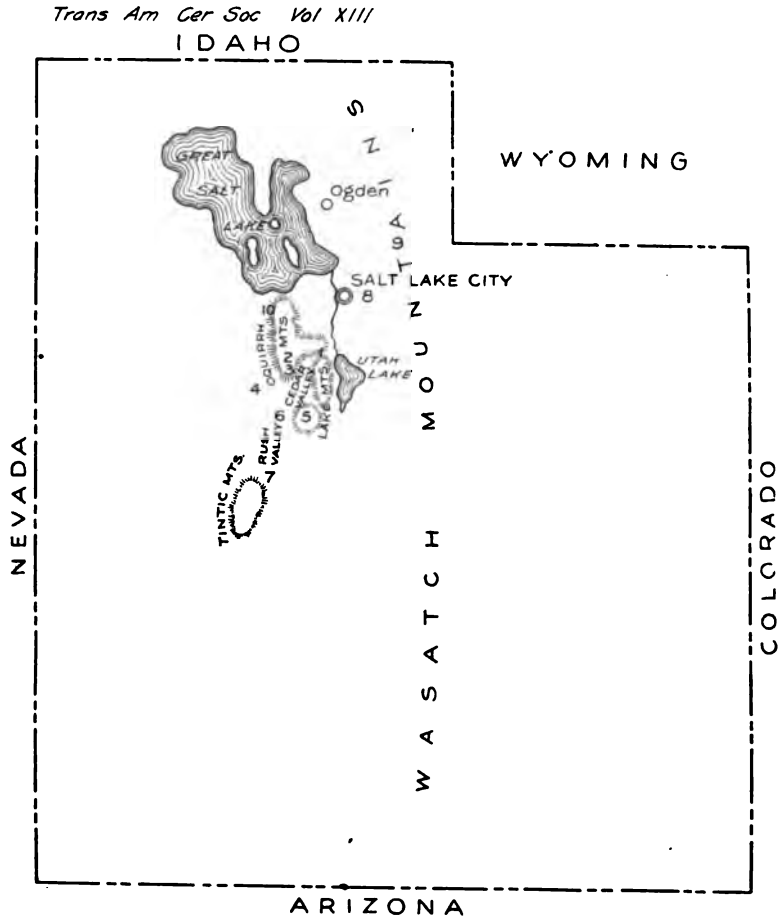

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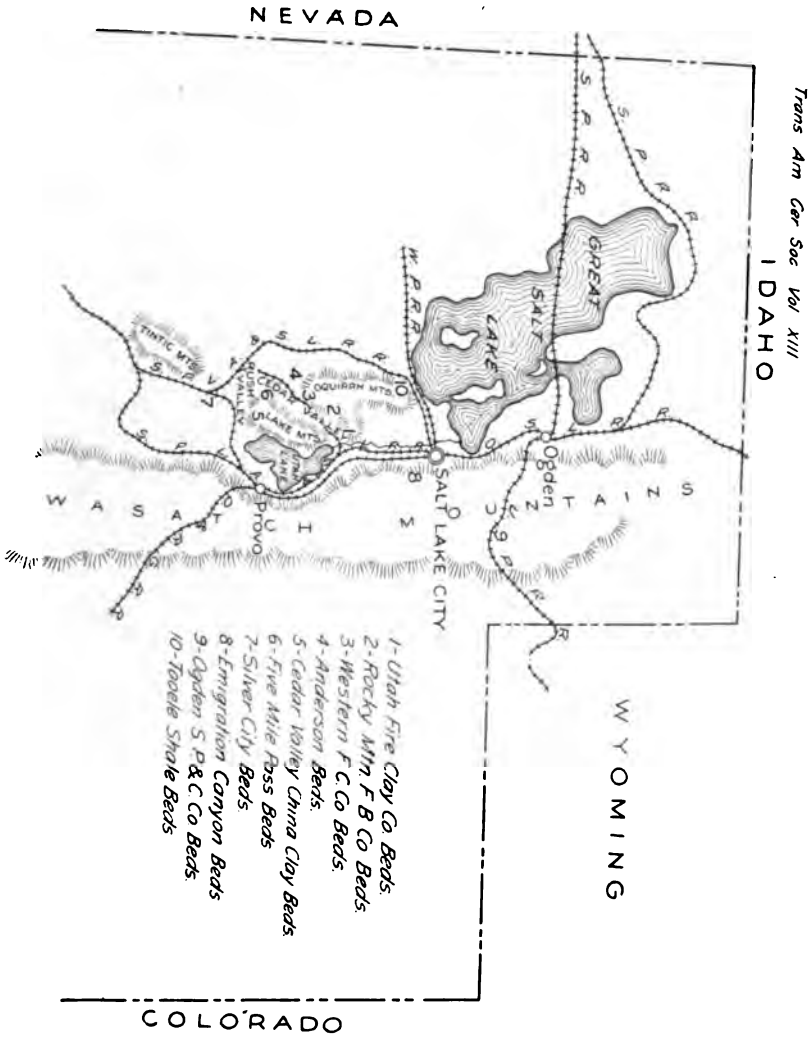

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mountain ranges traversing the state, slashed through and through as they are, by canyons that expose the stratification for thousands of feet vertically, many beds of clay would be exposed. With a few exceptions, however, this is not the case.

Most of the high-grade clay beds of the state are located in the hills and mountains surrounding the Cedar Valley Desert, namely, the Oquirrh and Lake Ranges.

Cedar Valley is located in Utah County, about 35 miles south of Salt Lake City and Great Salt Lake, and just west of Utah Lake. It is shut off from the lake by the Lake Range.

The majority of the strata exposed in the mountains surrounding this valley is of Carboniferous age. The Carboniferous in Utah is not coal-bearing, being composed of deep water deposits.

Fortunately the valley is traversed by a railroad, a branch of the San Pedro, Los Angeles and Salt Lake. This road runs as close as 600 yards to some of the beds, but as far as 12 miles from others.

The clays of this section are all shipped to Salt Lake City, a distance of from 35 to 50 miles by rail, and with one exception are hauled to the railroad by wagon.

For the reason that most of the better-grade clays are located in a desert country where water for manufacturing, and in some cases even for drinking purposes, is not available, none of the factories using these are located at the beds. This also makes labor unavailable. Then, again, the principal market is Salt Lake City and the towns immediately surrounding it, and it is much cheaper to ship the raw material to the market than the finished product.

As will be seen in the description of the various clays, even the best of them are rather poor when compared with the clays of the East, this being true especially with regard to the fire clays. However, the fact that they are the only ones available makes them high grade in that section.

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UTAH FIRE CLAY COMPANY'S BED.

The first bed to be opened in the Cedar Valley district was the one now owned by the Utah Fire Clay Co., of Salt Lake City. This bed was discovered about ten years ago and has been operated ever since.

The property is located five miles west of Lehi, Utah

Plate I.
Utah Fire Clay Co's. bed, showing face.

County, in Township 5 South, Range 1 West, Salt Lake Meridian.

The strata in this part of the valley belong in the Upper Carboniferous and the bed is tilted practically to the vertical.

Description of Clay.—Three kinds of clay are found in the bed. A clay, which was evidently a fire clay, but stained by deposition of iron carried into it by water, forms about 75 per cent. of the deposit. The balance is com-

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posed of two kinds of No. 2 fire clay, both of comparatively poor quality. All are shaley in structure.

The first-mentioned clay and practically all of the fire clay are mixed up together, the fire clay being that part of the clay in the bed that has escaped being stained. A thin vein of fire clay, from eighteen inches to two feet in width, is found just west of the hanging wall of the main

Plate III.
Utah Fire Clay Co's. bed, showing loading bins.

bed, running parallel with it. The clay in this small vein is unstained and is known as a "crucible clay." The fire clay in the main vein is separated from stained clay by hand-picking.

The stained or brown clay burns to a red color and reaches its greatest density between Cones 9 and 10. It does not vitrify, the absorption never getting lower than 2.5 per cent. or 3 per cent.

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The fire clay from the main bed is gray in color. It burns to a good buff color and takes an excellent flash. The clay from the narrow vein burns to a pleasing cream-white.

Dip, Length of Outcrop Thickness.—The bed dips 80° to the east. The outcrop can be traced for about two miles and runs northwest and southeast. The thickness of the bed varies. In some places it is at least 100 feet wide, in others not more than 30 feet.

Walls.—The hanging wall is a heavy black limestone, from 30 to 50 feet thick. The foot wall is also a limestone.

The mining is done by open cut. The working cut is located about 1 1/4 miles north of the railroad, and is connected to it by a switch.

Analyses of Clays.

No.	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Alk. (Diff).	TiO_2	Loss
52	56.3	27.2	6.0	1.2	0.9	2.0		6.4
53	50.1	23.1	15.0	0.9	0.2	4.7		6.0
54	61.0	25.6	2.3	0.1	0.9	3.0		7.1
55	58.0	29.8	3.0	1.0	0.3	0.7		7.2
56.....	44.08	31.84	3.2	0.5	0.9	3.2*	1.4	15.17

NOTE.—In all analyses, except where noted, alkalies are obtained by difference.

No. 52. Average entire face.
No. 53. Sample of stained clay.
No. 54. Average sample fire clay.
No. 55. Picked sample fire clay—shows maximum Al_2O_3 content.
No. 56. Sample from thin vein—"crucible clay."

Uses.—The stained or brown clay is used for making sewer pipe, fire-proofing, and building brick. It makes a good grade of fire-proofing, a poor grade of pressed brick, on account of poor color, and a poor grade of sewer pipe. The sewer pipe trouble comes from the fact that it does not vitrify and consequently will not take a salt glaze.

[1] Alkalies determined.

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The fire clay, No. 54 and 55, as will be seen, is rather poor for refractory purposes. When made up into brick it rarely stands better than cone 26 and it becomes very dense at low temperatures.

It, however, makes a beautiful flashed brick. The color is equal to anything in the country in that line.

The "crucible clay," No. 56, while not very refractory, makes up into a good grade of assay wares.

ROCKY MOUNTAIN FIRE CLAY COMPANY'S BED.

This bed is located near Cedar Fort, Utah County, in Township 5 South, Range 2 and 3 West. It lies about 15 miles west of the Utah Company's beds.

Plate IV.

Rocky Mountains Fire Brick Co's. bed, working cut.

The deposit, which is a fire clay, is the largest and best in the state. It belongs in the Middle Carboniferous.

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Like all of the other beds in this district, it is tilted. The working cut is located about 4 miles from the railroad.

Description of Clays.—The clay is a plastic fire clay, gray in color and shaley in structure. Two varieties of

Plate VI.

Rocky Mountain Fire Brick Co's. bed, view along vein.

clay occur in the bed, one being somewhat harder than the other. Several iron-stained streaks, a few inches in width, run through the bed. Both kinds of clay work to a splendid body, the softer making the closer of the two.

Dip, Length of Outcrop Thickness.—The bed dips 70° to the west. The outcrop can be easily traced for a dis-

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tance of 7 miles. The bed will average 20 feet in thickness.

Walls.—The hanging wall is an extremely heavy bed of black limestone, averaging about 100 feet in thickness. The foot wall is a thin bed of irony sandstone.

Mining is done by means of an open cut.

Analyses of Clays.

No.	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Alk (Diff)	TiO_2	Loss
48....	61.7	25.0	1.0	0.7	0.3	2.5		8.8
49....	60.1	26.3	0.9	0.7	0.2	1.1		8.7
50....	56.20	30.6	4.0	1.3	tr.	0.7		7.2
51....	58.99	30.71	0.57	0.7	0.4	0.94*	0.32	7.30
61....	46.7	34.6	1.85	0.4	0.3	105		14.2

No. 48. Average of working cut.
No. 49. Average of working cut.
No. 50. Average of face in cut 150 feet north of working cut.
No. 51. Average of shaft 60 feet deep, 1/4 mile south of working cut.
No. 61. Picked sample of soft "crucible clay."

Uses.—This clay is a fairly good refractory, in fact, the best among the Utah clays. Average samples melt above cone 30, and with careful selection, ware can be made that will stand cones 33 and 34. It retains a very open body at high temperatures. It takes a beautiful flash. Assay wares made from it are of the highest quality.

WESTERN FIRE CLAY COMPANY'S BEDS.

These deposits are located near Fairfield Station, Utah County, in Township 6 South, Range 3 Wes . They lie 5 miles south of the Rocky Mountain beds.

Two separate beds are worked on this property. Both are very close to the railroad.

These deposits belong in the Middle Carboniferous.

Description of Clays in Bed No. 1.—The clays in this bed are very peculiar. Strata of vivid colors—yellow, purple, rose and white—lie one on the other, sometimes

* Alkalies determined.

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holding true and distinct throughout the length of the exposed face, sometimes merging and twisting into each other. The clay has a sandy feel, and breaks into blocky

Plate VII.

Western Fire Clay Co's. bed, face of bed No. 1. Cut is made through footwall to lower bench level.

masses. Considerable of the bright coloring matter is of vegetable origin.

Dip, Length of Outcrop, Thickness.—The bed has a dip of 15° to the north, and the outcrop can be traced for about 1200 feet. On account of the peculiar manner in

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which the deposit lies, it is hard to determine its exact thickness, but it appears to be about 40 feet.

Walls.—Both the hanging and foot walls are of limestone. Open cut methods are used in mining.

Analysis of Clays, Bed No. 1.—Lower bench.

No.	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Alk. (Diff.)	Loss
14	78.8	11.5	1.8	0.7	0.7	1.7	4.8
15	65.9	16.8	5.5	0.4	0.8	3.3	7.3
16	62.9	20.0	4.7	0.6	1.1	3.2	7.5
17	68.6	16.2	4.3	0.7	0.8	2.7	6.7
			Upper bench				
18	49.2	14.1	9.9	10.5	0.9	2.2	13.2
19	62.8	13.4	12.1	0.7	1.6	2.6	6.8
20	61.7	21.3	4.3	0.7	0.8	3.3	7.9
21	74.3	14.4	2.1	0.7	1.2	2.3	5.0
22	62.9	17.6	6.0	1.4	1.3	2.5	8.3

No. 14. Average white clay.
No. 15. Average yellow clay.
No. 16. Average purple clay.
No. 17. Average entire lower bench.
No. 18. Average yellow clay.
No. 19. Average rose clay.
No. 20. Average purple clay.
No. 21. Average white clay.
No. 22. Average entire upper bench.

Uses.—As will be seen, none of this clay is high grade, and some of it is useless. However, by discarding such parts of the bed as the rose, No. 19, and the upper bench yellow, No. 18, the balance is put to valuable use. It is very easy to separate the clays in this bed as they have such distinctive, bright colors.

The white and purple clays are used as a bond for silica sand in making a clay-bond silica brick. These brick melt between cones 26 and 29, and work very well in many

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places, especially where subjected to a continuous heat and moderate temperatures.

This clay also makes a good grade of fire-proofing. It is most valuable however, in the manufacture of high-grade pressed face brick. It produces an almost endless variety of splendid colors, running through white, cream,

Plate VIII.

Western Fire Clay Co's. bed, upper bench of bed No. 1.

yellow, brown, purple, red and pink. The material takes a good salt glaze, but has never been tested thoroughly for sewer pipe.

Description of Clays in Bed No. 15.—This clay is a plastic fire clay of the usual gray to black color. The bed has several streaks of stained clay running through it. Its working qualities are good.

Dip, Length of Outcrop, Width.—The bed dips 30° to

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north. It outcrops along a southeast and northwest line for a distance of 1 3/4 miles. It varies in width from 3 to 10 feet, the average being 5 1/2 feet.

Plate IX.
Western Fire Clay Co's. bed, opening on bed No. 15.

Walls.—The foot wall is a soft limy clay. The hanging wall in contact with the clay is a red quartz stratum about one foot thick, above which is a bed of limestone.

On account of its dip and narrowness, this bed is worked by means of a tunnel, and the clay "stoped" from above.

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Analyses of Clays, Bed No. 15.

No.	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Alk. (Diff.)	Loss
1	60.9	25.0	3.1	0.5	1.1	2.5	6.9
2	59.9	26.6	2.3	0.3	1.0	2.9*	6.9
7	51.9	21.3	15.5	0.5	0.7	3.9	6.2
8	62.0	24.9	1.2	0.7	0.8	2.9	7.5
9	65.3	21.2	0.9	0.4	0.9	3.2	8.1
12	60.2	27.0	1.0	0.3	1.0	3.1	7.4
13	58.8	26.3	2.5	0.8	1.0	2.8	7.8
24	67.4	21.2	0.6	0.3	1.1	2.2*	6.9

No. 1. Upper $3^1/_2$ feet at working opening.

No. 2. Lower 2 feet—under No. 1.

No. 7. Red and yellow stained clay—streaks 1"–3" running through bed.

No. 8. $^3/_4$ mile east of where Nos. 1 and 2 taken—average.

No. 9.—200 yards east of No. 8—average.

No. 12. 50 feet west of Nos. 1 and 2—average surface sample.

No. 13. 50 feet west of No. 12—average surface sample.

No. 24. 700 feet west of Nos. 1 and 2—10-foot hole-average—bed faulted between this point and No. 1 and is 75 feet lower on hillside.

Uses.—The above analyses do not show the true quality of this bed. Most of the samples are from the surface, as very little development work had been done at the time they were taken. They are therefore, naturally high in fluxes.

This clay makes a fair grade of fire brick for that section and also a buff face brick.

The difficulty encountered in mining this clay makes it expensive and therefore prevents its use to any great extent.

ANDERSON CLAY BED.

This bed is located about two miles northwest of Fairfield Station at the mouth of Clay Canyon, in Township 6 South, Range 3 West.

This deposit belongs in the Middle Carboniferous.

The bed has been opened alongside the right of way of the Salt Lake & Mercur R. R.

* Alkalies determined.

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Description of Clay.—The clay is a good grade of plastic fire clay. It is gray in color, with here and there the usual iron-stained streaks running through it.

Dip, Length of Outcrop, Thickness.—It dips 60° to the north. The length of the outcrop and the thickness of the bed was not accurately determined. The outcrop is at least 1000 feet long and the thickness of the bed or series of beds is at least 30 feet.

Walls.—The walls were not found as the examination was made after a heavy snowfall. The indications are that they are limestone.

Analysis of Clay.

No.	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Alk.(Diff.)	Loss
57.....	59.8	29.6	1.6	0.4	0.4	0.9	7.3

No. 57. Sample taken from surface near R. R. track.

Uses.—This clay makes a good buff or flashed face brick and a fairly good dry pressed fire brick. The clay near the surface becomes dense at a low temperature, but this may not be the case when a greater depth is reached.

CEDAR VALLEY CHINA CLAYS.

This immense bed of white clay is owned, almost entirely, by the American China Clay Co. It covers an area of several square miles on the east side of Cedar Valley in the Lake Range, in Township 8 South, Range 2 West.

Nothing more than development work has been done on these clays. Their distance from a railroad has been very detrimental to them, the nearest loading station being 12 miles away, over a desert.

The formation probably belongs in the Upper Carboniferous, although the writer is not positive of this.

Description of Clays.—The clay is a high-grade china clay. Several colors occur in the bed—white, gray, red and yellow, the white, by far, predominating. The colored clays are useless, but as they occur in separate strata, the good and bad clays are easily kept separate.

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The working properties of the clays are good. They are very plastic, so much so that they would be used in a white body to replace the ball clay. They are very fine-grained, passing through the finest lawns. In the bank, the clays have a chalky appearance and break up into blocky masses.

Dip, Length of Outcrop, Thickness.—The dip is 20° to the south. The deposit is cut in a large number of places by canyons and washes and can be traced for a number of miles in this way.

Its thickness can only be estimated. From 18 to 20 feet of white clay, capped with 3 1/3 feet of red, appears at the largest opening on the bed. It has been variously estimated that the bed is from 50 to 200 feet thick.

Walls.—Only the hanging wall can be seen. It is a stratum of sandstone about 10 feet thick. The mining can be carried on for the present by the open cut method. The overburden is generally heavy.

Analyses of Clays.

No.	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Alk.(Diff.)	Loss
32	47.5	39.2	0.7	0.6	0.5	...	12.5
33	51.5	29.6	3.6	1.3	0.7	1.4	11.7
34	51.6	24.3	3.6	1.4	1.2	2.8	14.9
58	46.3	39.5	tr	tr	tr[1]	tr[1]	13.4

No. 32. White clay—best—average.

No. 33. Red clay above white

No. 34. Gray clay from surface, taken two miles from where No. 32 was taken.

No. 58. Sample of best white clay after free silica had been washed out.

Uses.—The white clay burns to a beautiful clear white. Its shrinkage is great—20 per cent. at cone 13. As will be seen, it has practically the composition of kaolinite, when washed, and is very pure in the unwashed state.

[1] Alkalies determined.

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Carloads of this clay have been shipped to different parts of the country to be tested and it has in each case proved to be valuable. The writer has seen several samples of porcelain, produced in an experimental way, which were excellent, in which this clay formed the entire clay ingredient.

The red clay, which occurs between the hanging wall and the white clay, is useless. It burns to an undesirable red color and has as great a shrinkage as the white.

FIVE-MILE PASS CLAY BEDS.

Just south of Cedar Valley is Rush Valley. At the northern end of this valley is located the Five-Mile Pass bed. This bed lies about 5 miles southwest of Fairfield Station, partly in Utah and partly in Tooele Counties, in Township 7 South, Range 3 West. The railroad cuts the outcrop.

Unlike the other beds described, this one outcrops in the valley bottom, and the clay is mined through an inclined entry.

The formation belongs in the Middle Carboniferous. It is tilted as usual.

Description of Clay.—The clay is a sandy, plastic fire clay, of the usual color except for a band of stained clay about three feet wide which runs through most of the bed about two feet under the hanging wall.

Dip, Length of Outcrop, Thickness.—The bed dips 20° to the southwest. The outcrop can be easily traced for three quarters of a mile, the overburden being thin over that distance.

It was impossible to measure the thickness of this bed, as the foot wall could not be found. The development work done, however, shows that it is at least 25 feet thick.

Walls.—The hanging wall is a heavy black limestone that makes a good roof. The foot wall does not show.

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Analyses of Clays.

No.	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Alk. (Diff.)	Loss
25.....	62.3	24.4	1.0	0.4	0.6	1.6	9.7
27.....	72.1	18.1	0.4	0.3	0.8	2.3	6.0
28.....	72.5	18.8	0.5	0.3	0.8	1.1	6.0
31.....	61.1	22.6	4.6	0.5	0.6	2.2	8.4

No. 25. Bottom of entry, near floor—200 feet from surface.
No. 27. Half way up inclined entry—average of face.
No. 28. One-third distance from mouth—average of face.
No. 31. Average of stained clay.

Uses.—This clay makes a very desirable face brick in a number of buff shades. The iron it contains is in nodular form and makes a pretty iron spot.

It burns to such a dense body at low temperatures that it is useless for refractory purposes.

SILVER CITY CLAY BEDS.

These beds are located about nine miles west of Silver City, Juab County, in Township 11 South, Range 4 West. They are located in a country that is practically all porphyry, belonging in the Tertiary. The clay beds are probably the result of the decomposition of the porphyries.

They are located at a considerable distance from a railroad, about 12 miles by road, and have practically been abandoned since the discovery of the Cedar Valley clays. This clay was, however, the first, other than the surface clays, to be used in the state.

Description of Clays.—The clays have a blocky structure. They are white, light green and light yellow in color. They are very fine-grained and very plastic.

One of its peculiarities is that it has absolutely no shrinkage even at high kiln temperatures. The body remains very open and punky.

Dip, Length of Outcrop, Thickness.—There is no dip to the beds. It is a blanket formation, apparently the filling of small ponds in very recent geological times. The deposit is large in area and apparently quite thick.

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Analyses of Clays.

No.	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Alk (Diff.)	Loss
45	68.0	24.3	1.0	tr.	tr.	0.7	6.0
46	72.8	15.0	4.0	0.25	0.2	0.75	7.0
47	70.0	23.6	1.4	tr.	tr.	tr.	6.0

No. 45. Sample of white from opening from which clay was first mined.
No. 46. Sample of white from last opening used.
No. 47. Sample of green clay.

Uses.—This clay was used for the manufacture of refractories, but was not a great success.

It might prove useful in a white ware body, especially as it has no shrinkage and burns to a pure white.

EMIGRATION CANYON CLAY BEDS.

Several beds of shale outcrop in this canyon. The principal bed is located about 1 3/4 miles from the canyon

Plate XI.
Emigration Canyon bed, slope in foreground is all shale.

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mouth and about 6 miles from the center of Salt Lake City, in Salt Lake County. An electric railway system runs through the canyon.

The geological age of this clay was not determined.

Plate XII.

Emigration Canyon bed. Mountain in background practically all shale.

Description of Clay.—The principal bed, and the one here described, is a hard gray shale. It is fine-grained, but so hard that it requires a good pugging to make it workable. It, however, becomes very plastic.

Being very high in lime, it does not burn to a dense

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body, but at temperatures between cones 1 and 4 it becomes very hard and gives a good ring. It has a good burning range and can safely be taken up to cone 7 before showing the first signs of fusion. It produces a brick of an excellent cream-white color. It has no shrinkage up to cone 4.

Dip, Length of Outcrop, Thickness.—The bed dips 60° to the northwest. It is an immense body of shale about 2000 feet thick, and can be traced several miles northward from the canyon bottom.

Walls.—The hanging wall is a black limestone and the foot wall a red clayey sandstone.

Analysis of Clay.

No.	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Alk. (Dif.)	Loss
59.....	25.4	6.0	8.0	30.2	3.0	tr.	27.3

No. 59. Average sample.

Uses.—This clay makes a brick of a very desirable color. It is very light in weight, a brick of common building size weighing about 3 1/2 pounds.

OGDEN SEWER PIPE AND CLAY COMPANY'S BED.

This bed, which contains the best red burning, vitrifying clay yet discovered in the state, is located at the head of Owen Canyon, a branch of Echo Canyon, in Summit County. It lies about 35 miles east of Ogden.

The bed is located at the top of the mountains and is difficult of access, but for years the clay from it has been hauled a distance of 5 miles, to the railroad, by wagon. It is shipped to Ogden.

Description of Clay.—The clay is red and white in color and has a very sandy feel. It is easily worked up and becomes very plastic. When burned, it has an excellent cherry-red color and vitrifies to a body that cannot be excelled. It takes a good salt glaze very easily.

Dip, Length of Outcrop, Thickness.—It dips 12° to the west. The outcrop cannot be traced more than a few

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hundred feet, and it is probable that the bed is heavily covered except at the mountain top where it is opened.

A 40-foot face is exposed, but it is probably much thicker. The overburden prevents any accurate measurements.

Walls.—It was impossible to determine the kind of walls, either top or bottom.

Analysis of Clay.

No.	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Alk. (Diff.)	Loss
60.....	64.6	16.0	6.3	0.61	0.5	4.0	7.5

No. 60. Average sample of face.

Uses.—This clay makes excellent sewer pipe. The body is of good color, is dense and takes a good glaze. Some trouble is experienced in making pipe from 18 inches upwards. The clay is not strong enough to carry the weight of the large-sized pipe after the "former" has been removed. Care must also be taken in the burning, as the vitrification range is not great.

OTHER CLAY BEDS.

The above covers all of the clay beds in the state that have proved themselves of value to the clayworkers. Many other beds have been reported in nearly every portion of the state, but as yet their value to the clay industry has not been investigated. Many of them can never be of value for many reasons, chiefly their geographical location. As would naturally be supposed, fire clays are found under the great coal beds of Carbon, Emery and Summit Counties. Many of these have been tested by the writer, among them some good-looking flint fire clays, but none of them have shown up very well. In the writer's estimation, a thorough examination would reveal some good clays in these coal fields.

Immense bodies of shale have been reported in the southeastern counties, San Juan, Grand, Kane, Garfield

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and Wayne, but as the greater part of this country will always remain an untouched wilderness, they are not very likely to become of value. White clays of doubtful value are found in Millard, Sevier, Piute and Beaver Counties.

Large shale beds, that will undoubtedly prove valuable, have recently been developed between Tooele and Milton in Tooele County. The clay looks very much like that of the Utah Fire Clay Co., some of it being brown and some gray.

Beds of clay will be opened from time to time, but for a long time to come the number of useful ones is bound to be limited.

Note.—Analyses used in this paper were made by Prof. W. C. Ebaugh, University of Utah; R. H. Officer & Co., chemists; and by the writer.

The writer is grateful to Mr. L. L. Nunn for allowing the use of some of the analyses and of information obtained while in his employ.

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NOTES ON CHROME-ALUMINA COLORS.

By A. S. WATTS, Columbus, O.

Professor Marquardt, of the Versuchs Anstalt to the Royal Porcelain Works, has several specimens of chrome-alumina colors which by daylight, however, are nearer a purple than a pink. This being rather a unique phenomenon, I undertook a study of the composition of these with an idea of their possible use as underglaze colors. The study as made was divided into three series:

Series I.—Aluminium hydroxide and chromic oxide ground together and calcined.

Series II.—Aluminium hydroxide, chromic oxide and boracic acid ground together and calcined.

Series III.—Aluminium sulphate and potassium bichromate dissolved together in hydrochloric acid and precipitated together by ammonium hydroxide in the presence of alcohol.[1]

SERIES I.

Series I was a study of the effect of variation in percentage quantities of $Al(OH)_3$, starting with the following mixture as Member 1, and gradually increasing the proportion of $Al(OH)_3$ in each succeeding member.

Member 1.....	$Al(OH)_3$	73.81%
	Cr_2O_3	26.19

One set of mixtures of this series was calcined at cone 18 in a gas furnace, and another at cone 22 in an electric furnace.

The first pink colored powder obtained in this series was of the following composition:

Raw		Calcined	
$Al(OH)_3$	93.48	Al_2O_3	90.53%
Cr_2O_3	6.52	Cr_2O_3	9.47

[1] The precipitate was sky-blue in color, probably being a chromous rather than a chromic hydroxide.

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Calcined at cone 18 this stain is a pinkish gray powder and at cone 22 it is a purplish gray powder.

SERIES II.

Starting with the following as Member 1 of this series,

$Al(OH)_3$	70.83%
Cr_2O_3	12.5
H_3BO_3	16.67

the succeeding members were made with increasing proportions of $Al(OH)_3$, obtaining, finally, a pink stain of the following composition:

Raw		Calcined	
$Al(OH)_3$	85.42%	Al_2O_3	83.62%
Cr_2O_3	6.25	Cr_2O_3	9.34
H_3BO_3	8.33	B_2O_3	7.04

Calcined at cone 18 in the gas furnace this stain is a pinkish gray powder and at cone 22 in the electric furnace it is purplish grey.

SERIES III.

This series was started with a powder of the following composition:

$Al_2O_3 + 3H_2O$	75.18%
$Cr_2O_3 + 3H_2O$	24.82

By adding $Al(OH)_3$, and calcining at cones 18 and 22 as before, the following pink powder was finally obtained.

Raw		Calcined	
$Al(OH)_3$	84.2	Al_2O_3	82.26%
$Cr(OH)_3$	15.8	Cr_2O_3	17.74

Calcined at cone 18 this stain is pinkish gray, and at S. K. 22 it is lavender gray.

Testing of the Stains.—These three pink stains were tried under the following glazes:

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Glaze A:	0.3 K_2O 0.7 CaO	0.7 Al_2O_3	5.0 SiO_2
Glaze B:	0.5 K_2O 0.5 CaO	0.7 Al_2O_3	7.0 SiO_2
Glaze C:	0.3 K_2O 0.4 CaO 0.3 BaO	0.9 Al_2O_3	9.0 SiO_2
Glaze D:	0.3 K_2O 0.4 CaO 0.3 ZnO	0.9 Al_2O_3	9.0 SiO_2
Glaze E:	0.3 K_2O 0.4 CaO 0.3 MgO	0.9 Al_2O_3	9.0 SiO_2

All the glazes were fired at cone 14 in a small trial kiln.

Results.—The results of the glaze trials indicated that the powders calcined at cone 18 were much more pink than those calcined at cone 22.

The stain from Series II seemed to give the best color, with that from Series I as a close second, while the one from Series III gave a very pale color indeed.

Attempts to improve the color of Series I by increasing the aluminium oxide content proved futile.

Effect of B_2O_3.—Replacing a portion of the Al_2O_3 with B_2O_3, a pink stain was obtained which had the following composition:

Raw		Calcined	
$Al(OH)_3$	89.06%	Al_2O_3	87.64%
Cr_2O_3	4.69	Cr_2O_3	7.06
H_3BO_3	6.25	B_2O_3	5.31

Effect of ZnO.—By replacing the B_2O_3 with ZnO, a fine pink color of the following composition was obtained:

Raw		Calcined	
$Al(OH)_3$	86.93%	Al_2O_3	81.30%
Cr_2O_3	6.10	Cr_2O_3	8.70
ZnO	6.97	ZnO	10.00

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Further increase of ZnO developed a delicate peach blow pink color with no trace of purple. This stain had the following composition:

Raw		Calcined	
$Al(OH)_3$	81.26%	Al_2O_3	73.925%
Cr_2O_3	5.70	Cr_2O_3	7.935
ZnO	13.04	ZnO	18.14

Effect of ZnO and B_2O_3 Together.—When ZnO and B_2O_3 were used in the same stain, the effect of ZnO was noticeably weakened by the presence of B_2O_3.

TiO_2 Versus B_2O_3.—TiO_2 was substituted for B_2O_3, obtaining in the following a peculiar purplish brown, quite similar to the manganese-brown in raw lead glazes.

Raw		Calcined	
$Al(OH)_3$	86.93%	Al_2O_3	81.30%
Cr_2O_3	6.10	Cr_2O_3	8.70
TiO_2	6.97	TiO_2	10.00

Practical Possibilities of These Stains.—All the above stains were ground with equal parts kaolin and put on porcelain biscuit as underglaze colors under the above-mentioned glazes, there being no apparent injury to color in any case. Attempts to use these colors under soft white ware glazes, however, have failed, and there may be other difficulties to be overcome in adjusting them to low temperature use, but for firings at cone 12 to 16 they appear to be thoroughly practical.

DISCUSSION.

Mr. Stover: Probably the trouble in your experiments with Mr. Mayer was in the soft glaze, rather than in the soft fire. I have proven that the difficulty in producing a chrome-tin stain at high heats was with the ingredients in the glaze, rather than the high fire. With the proper glaze, cones 11 and 12 could be reached without detrimental effect on the color.

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Mr. Burt: Did you get any development of pink under 18?

Mr. Watts: I got a tendency toward pink at cone 16, but at less than 18 there was no satisfactory pink-gray powder. It had a flat, pale (silver or lavender) tint.

Mr. Stover: Did you calcine your powder under oxidizing conditions?

Mr. Watts: Yes.

Mr. Stover: You did not try them under reducing conditions?

Mr. Watts: I got a bright chrome-green under reducing conditions.

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NOTES ON ROOFING TILES AND THEIR MANUFACTURE.

By CHARLES STOLP, Chicago Heights, Ill.

Probably no other roofing material is superior to clay tiles, and although this is generally conceded, they are not used in America as extensively as one could expect from the largeness and the prosperity of this country. Europeans have manufactured clay tiles for hundreds of years and to-day they find a much more extensive use abroad than here, both in actual amounts and in proportion to the number of buildings erected.

Clay roofing tiles may be classified from several view points and perhaps a complete or exhaustive classification would of necessity include all of these as follows:

Vitrified Non-vitrified Glazed	Interlocking Non-interlocking	shape.

Vitrified tiles are easy sellers, *i. e.*, they commend themselves to the purchaser because if impervious to water they would not place the roof structure periodically in excessive strain as the porous tiles would possibly do when saturated. As a matter of fact these sort of arguments are unfounded. Water from rains or melting snow will not drain through the most porous of tiles and the water which would be soaked up by porous tile, even in our most prolonged wet seasons, would not be sufficient to saturate the tile. After the exterior surface of a porous tile becomes saturated, most of the water which falls on to it would run right off of the roof. On the other hand, steam and moisture from the interior of buildings will collect on clay tile (they being cool on account of their low specific heat) and, if the tile are porous, this moisture will be absorbed and eventually evaporated through the outside surface, while if the tile are vitrified, the sweat will accumulate and finally drip from the interior surface of the roof. It would not be difficult to prove that there is no advantage to the purchaser in vitrified tile.

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When it is considered that to vitrify a tile requires more fuel and entails a heavier loss due to warping, etc., it is easy to see that vitrification of the tile would of necessity make them more expensive and this too without making them better roofing material.

The primary reason for glazing clay roofing tiles is to produce colors that can not be obtained from natural clays. It adds cast and gives an impervious surface to the tile; hence they command a larger price.

To prevent overlapping of the tile, thus cutting down the weight of a roof, the tiles are very often made so as to interlock. Along by one edge of the interlocking tile is a tongue and along the other there is a groove just as in tongue and grooved lumber, with the exception that this tongue and groove in place of being on the side or edge, the tongue is on the under side and the groove on the upper side of the tile. The flat shingle tile are laid exactly as are the wooden shingles; they do not interlock.

There have been a great many patents issued covering special shapes for roofing tiles, in fact such patents have been sold outright or exchanged for considerable stock. But notwithstanding all of this, the bulk of the trade is now and always will be restricted to the few standard shapes. There is no particular value in these other special shapes other than what the patentee may receive for his patent. According to the standard shapes, tiles may be sub-divided into:

(*a*) Corrugated flat tiles.
(*b*) Flat shingle tiles.
(*c*) S or Spanish tiles.

The number of tile of each of these groups required to cover a square are as follows:

(*a*) Corrugated flat	135 to 125
(*b*) Flat shingle	400
(*c*) S or Spanish	160 to 180

The color of tiles is usually either red or green. The red is either the natural color to which the clay burns, or

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to which the clays burn which are used as slips. The green is produced in matt glazes by copper.

The most desired color for tile is the deep rich red, but the trade asks for nearly all the shades and colors produced by terra cotta manufacturers. For browns, the roofing tile manufacturer resorts to iron ore and manganese.

The clays used in the manufacture of roofing tile should be such as will flow well in the die, not only of the auger machine, but in the presses. They should also burn to a good red color and with little warping. It is to be preferred that the clay should have a considerable heat range over which it holds its color and shape. Unfortunately, however, most factories are not now using the clays which are best suited for manufacture into roofing tiles.

Because of the intricate shapes in some, and very thin section in all instances, the clay should be so handled as to develop its best working properties. To this end we find that many of the shales must be weathered. The object of weathering of course is to obtain disintegration, but if in case the clay should contain compounds which would be rendered soluble by weathering, and thus cause scumming, the manufacturer would perhaps have to forego the benefits of weathering.

Since the clay in most every deposit so varies in character as to cause differences in shrinkage, color, etc., it is important that an ample stock shed be provided in which the clays from the different strata can be thoroughly blended.

As easy flow under pressure without structural defects is probably as important, if not more so, in the roofing tile manufacture as in any other clay industry, the ratio between weight of the dry pan mullers and screen plates should be such as to give the maximum grinding effect. Fine grinding of the clay is important. In fact the clay should be so ground as to pass a 20-mesh stationary woven wire screen pitched to 45° angle.

In the case of loose clays which are apt to be more or less wet, rolls have been used, but since the rolls wear

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so rapidly, this method of granulation is rather expensive. For such clays, a hammer or rotary disintegrator is the most serviceable.

In some cases I have found that the clay should be so preheated as to drive out all of the mechanical water. In this way we not only obtain easier granulation but better drying behavior.

After the clay is ground and rendered plastic by pugging, roofing tile manufacturers have found benefits in storing the clay in soak pits for a while before using, and especially is this true when manufacturing the interlocking tiles on a press. This not only produces an easier working clay for presses but it gives opportunity to again homogenize the mixture.

For the making of plain tile on an auger machine, the clay should be stiff, but for the clay clots from which more complicated shapes are pressed, the clay should be as plastic as possible and still not give difficulty in the handling. This is a very important thing to watch for the men much prefer the clay as stiff as possible.

The difficulty in working the clay stiff on a press is the fact that the laminations, produced in the clot bar by the auger machine, and the crevices, produced in the pressing, make the tile susceptible to disintegration by frost.

If the shape is such as can be produced on an auger machine, the tiles will be run out and cut off much the same as are stiff mud bricks. If the shapes are complicated, as in case of the interlocking tile, they must be made on a power press. For this, clay is caused to issue in a soft state in the form of a bar from an auger machine and cut into appropriate lengths, producing what is known as clots.

For a capacity of 40 square per day, I advise the use of a hexagon press because they have greater capacity and produce just as good results as the single die presses. Since perfect surfaces at the least expense are most desirable, a close study of the metal best suited for the die of these presses is important. For some purposes and with some

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clays the plaster dies are more valuable than the metal dies, and for the metal dies some clays require that special steel or cast irons be used. This, however, is a problem that requires special attention for each clay.

Roofing tiles are dried in exactly the same manner as are bricks.

For burning vitrified tiles they use pigeon holes formed by fire clay slabs. The slabs are usually about 16″ x 12″ x 2 1/2″.

If warping is likely, as is generally the case in the Spanish tiles which are shaped like the letter S, they are set nested on ribbons of soft clay and are bound at the top surface by a similar ribbon of soft clay.

For the burning of porous tile, they use much the same sort of setting as in brick, the tile being always set on end. In a row of about 14 feet between the bag walls we usually put in two headers, setting the tiles scantling on top of one another to prevent the upper courses from telescoping into those below.

Nearly all types of kilns are used for burning roofing tile but I prefer the rectangular down draft. They should not be more than 14 feet between bag walls and not higher than 9 feet. The fire boxes should be 6 1/2 to 7 feet between centers.

Of course a continuous kiln is to be preferred, but these would require a daily capacity of 6000 tile regularly the year around in order to obtain the full benefits from their use. One auger machine on the Spanish tile or one press would keep a continuous kiln supplied with tile for burning.

In closing I wish to draw attention to a very valuable treatise on roofing tile by Worcester and Orton, which was recently published by the Ohio Geological Survey.

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THE CONSTRUCTION OF A CENTER-STACK DOWN-DRAUGHT KILN.

By E. T. MONTGOMERY, Urbana, Ill.

Introduction.

In this paper no attempt will be made to compare types of construction. It will be merely a description of the construction, and a discussion of the merits, of a very

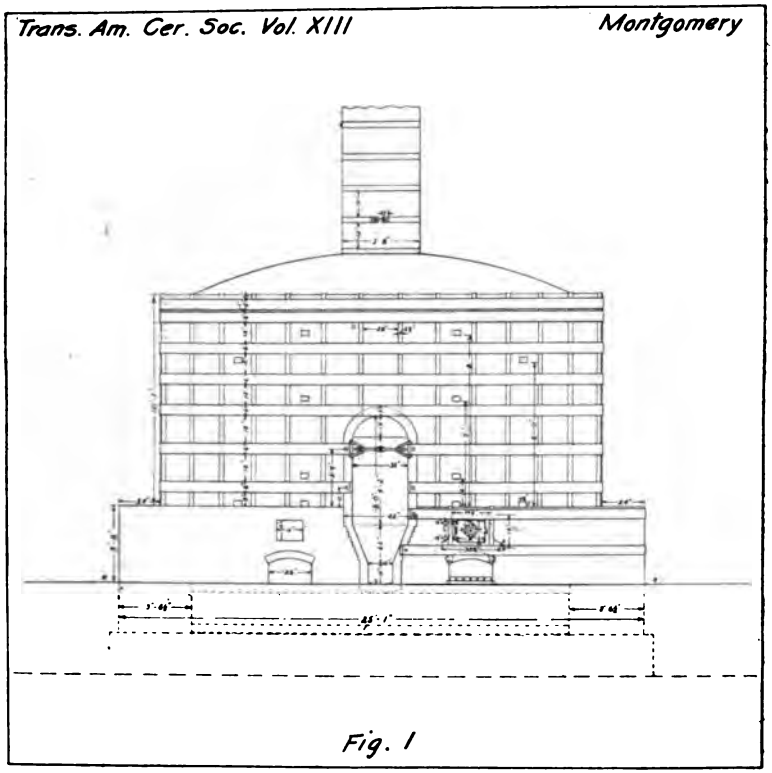

Fig. 1

satisfactory and successful center-stack down-draught kiln which the writer has used in practice and which he can commend to your use for stoneware, enameled brick, electrical porcelain, floor and wall tile, white ware or in fact

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any kind of clay product that can be economically burned in a round kiln and where the position of the stack in the center of the kiln will not seriously interfere with a car system of unloading if that system be used.

I trust that some of the advantages of construction,

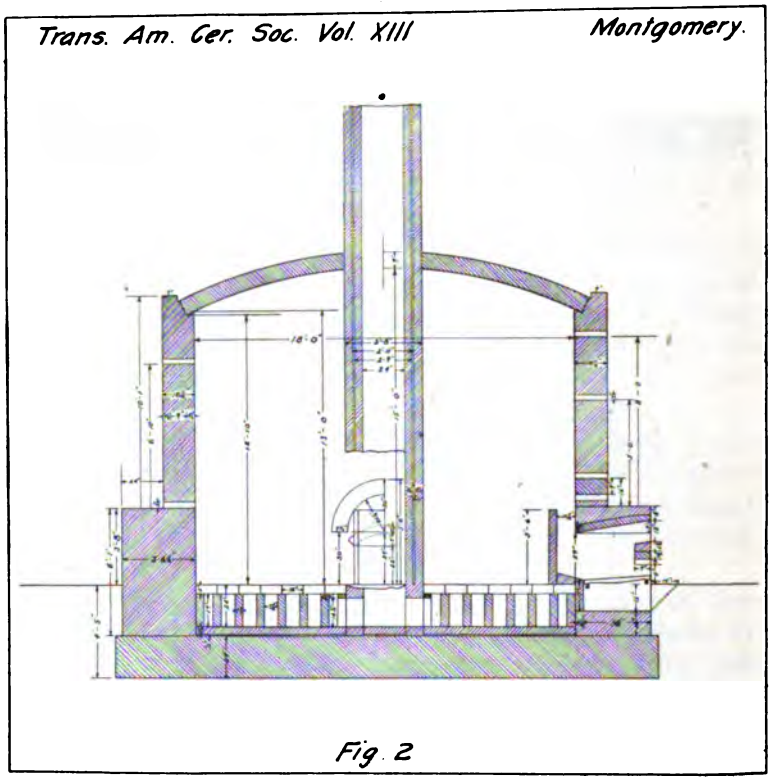

Fig. 2

the efficiency, and the economy of fuel consumption of this kiln, will appeal to you and increase in the industry the use of a kiln that, as far as my experience and observation goes, has "made good" wherever adopted, and which I believe, with the application of the continuous principle which we will discuss later, will be, at least until we are ready to adopt the continuous or tunnel kiln of Europe, the kiln of

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the future in its particular field; and that field I am fully convinced, will overlap the present day up-draught potters kiln now used in practically all of our white ware plants.

Another reason for this paper in the form in which it is given is that it is high time we were getting into our

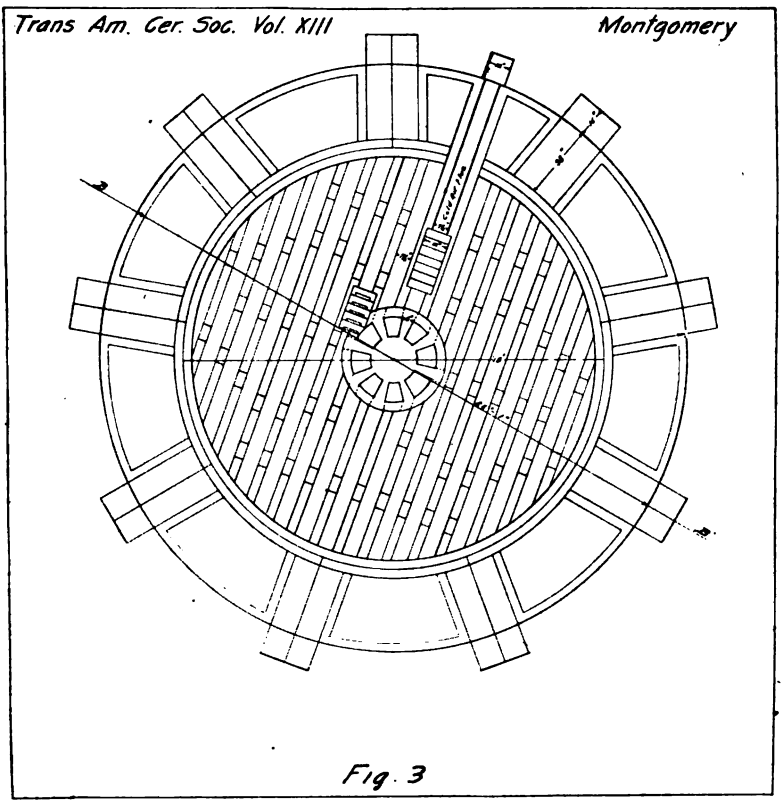

Fig. 3

ceramic literature some exact designs of kilns with measurements and dimensions that can be used in the construction of kilns elsewhere, or in discussion of improvements. It is only in this way that we will ever be able to efficiently compare our kilns and eradicate some of the doubtful construction that is sometimes used through just this lack of efficient means of comparing notes.

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Inside Discussion.—The kiln I will describe is 18 feet inside diameter, by 13 feet to the spring of the crown and has a center stack 3 feet 9 inches in diameter (outside). The rise of crown is 2 feet 2 inches.

Foundation.—The foundation is of concrete and about 12 inches thick on hard, well tiled soil. It is carried out under each ash pit as well as under the kiln proper. This foundation insures a solid, level and dry kiln bottom.

Flue System.—The flue system is best shown by the drawing which almost explains itself. There are 17 horizontal parallel flues 7 1/2 inches wide by 19 inches deep to the concrete foundation. The system of arches through the flue walls are arranged in a Fig. 8, together with 3 other rows of arches at right angles to the flues. This design has given excellent results in connection with a properly proportioned checker floor over the flue system. In this checker floor the openings should increase in number or size from the stack out to the wall. You will note that the line of the direction of the flues is at an angle to the line from the center of the door to the center of the stack. This was done so that the covered flue to the stack would not conflict with the fireboxes. This flue could be put under the flue system, in which case the line of door, stack, and firebox No. 5 could be made parallel with the flue walls. The flue walls are 4 1/2 inches wide and are 12 inches center to center so that they take a checker floor brick of 5″ x 12″ face. There are 8 arched openings into the bottom of the stack and they should be made deep enough so that their total area is equal to the area of the stack. The covered flue has a damper outside of the kiln, and is used to cool the center of the kiln during the later part of the burn and drive the heat to the outside if necessary. It can also be used as a damper as the draught through the kiln is lessened when this flue is opened and allowed to draw cold air direct from the kiln room.

Fireboxes.—The fireboxes are 9 in number and equally spaced about the hob except at the door, where a little extra space is required to get the door in. This extra

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Trans. Am. Cer. Soc. Vol. XIII Montgomery

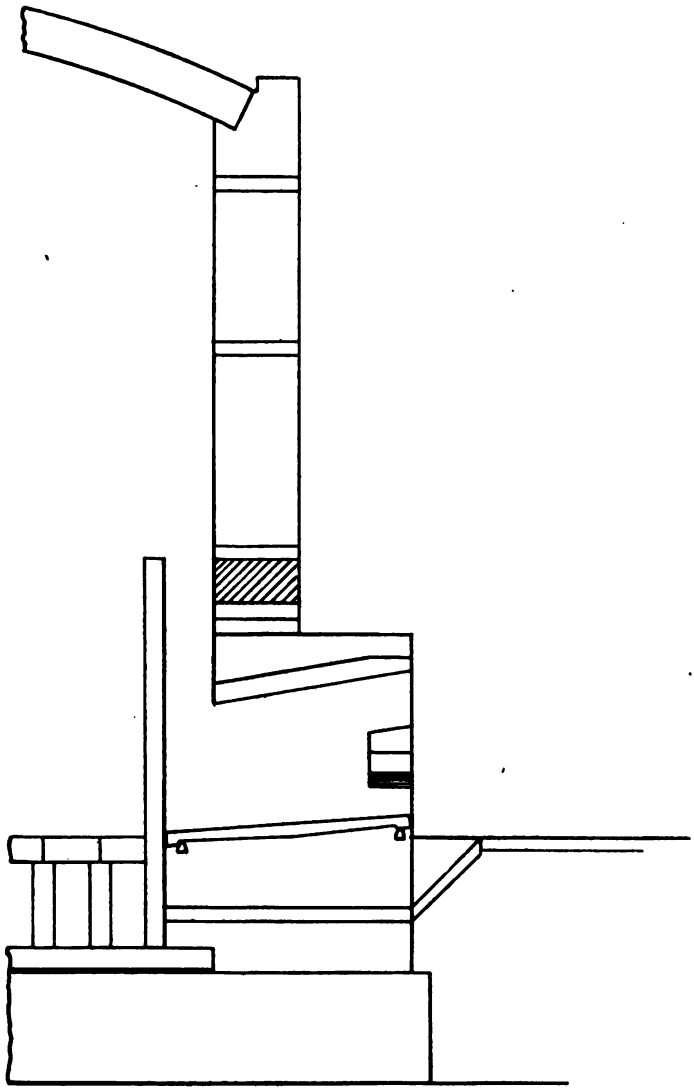

Fig. 4

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distance from center to center of the fireboxes on each side of the door should, for obvious reasons, be made as small as possible. With the one exception, the distance from center to center of fireboxes on the outside wall is 8 feet 3 inches. The drawing shows the section through the hob, firebox, ash pit and bag. The bag walls extend down to the concrete foundation and the grate bars are 4 feet 5 inches long, reaching to the back of the bag and resting on a cross bar set to receive them. The long bars have the advantage of keeping the mouths free from clinker and they also make the mouths easier to clean after the bars are dropped, there being no place for the ash and clinker to lodge, as in the case of the short bar used with a bag extending only to the kiln floor. Cutting out the clinker on the floor at the bottom of a short bag is very difficult to accomplish and also very hard on the kiln. Of course, with a long bag reaching to the foundation, we lose the value of a flue under the bag, but with a good large opening between each bag in the checker floor, I have experienced no difficulty with cold spots at these points.

Thickness of Walls.—The walls are 3 feet 6 1/2 inches thick through the hob and are 18 1/2 inches thick above the hob. The kiln is lined with one course of fire brick tied by headers to the red brick wall. All firebrick in the walls and stack are laid in fireclay mortar, soaked in water before placing and laid with very close joints. The outside walls are laid up in cement mortar and with close joints also.

Crown.—The crown of a kiln should always be the arc of a circle and in an 18-foot kiln the rise should be about 2 feet 6 inches. A crown should always be laid with a radial sweep or gauge, and the best one to use is one so constructed that the brick are laid against its end, the gauge being moved around the crown as each course is laid and keyed in. Photograph No. 1 shows this method very nicely. Here the brick mason is working from below as the crown is a lining under a crown already in position. Photograph No. 2 shows the correct way to use such a gauge.

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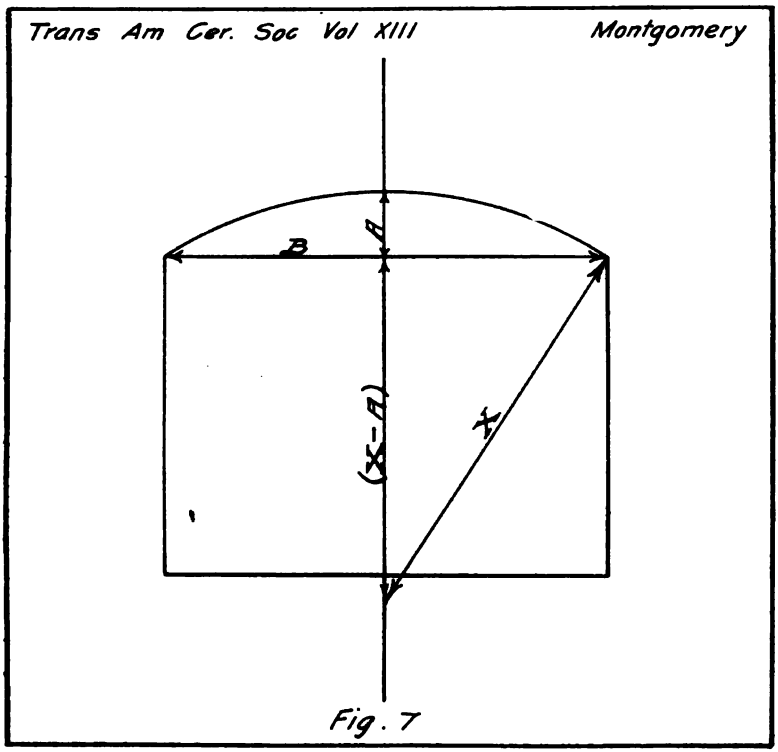
two men working from the top. One man and his helper can lay, by this method, 3000 brick in a crown in 8 hours and at the same time lay a perfect and solid crown. The construction of such a sweep or gauge has been described



before so I will only repeat here, for the sake of completeness, the method of figuring the length of the gauge. Let A = the desired rise of crown, B = the inside diameter of the kiln, and X = the length of the sweep. To find X in the triangle of which X is the hypothenuse we have:

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$$X^2 = (X - a)^2 + \left(\frac{b}{2}\right)^2$$

$$X^2 = X^2 - 2ax + a^2 + \frac{b^2}{4}$$

$$8ax = 4a^2 + b^2$$

$$X = \frac{4a^2}{8a} + \frac{b^2}{8a}$$

$$X = \frac{a}{2} + \frac{b^2}{8a}$$

or in words—the length of the sweep is equal to half of the desired rise of the crown plus the quantity equal to the diameter of the kiln squared, divided by eight times the desired rise.

Stack.—The stack is double-walled with an air space between. The inside stack is 24 inches in diameter inside and the outer one is 36 inches in diameter inside. The stack extends about 15 feet above the crown and terminates in a stack damper.

Cooling Vents.—For the purpose of more rapid cooling the kiln is provided with two crown plugs, as shown in the drawing, which can be removed, thus connecting the vents by pipes to an exhaust fan which draws out the hot air from the top of the cooling kiln.

Banding.—As the drawing shows, the kiln is well banded both horizontally and vertically. Vertical banding is most essential to keep the horizontal bands from cutting into the kiln, and to prevent lateral shifting due to expansion and contraction. The top horizontal band should, of course, lap the top course of brick.

Center versus Outside Stack.—This about covers the details of construction, and before making a summary I wish to say that I am not advocating primarily the center stack *versus* the outside stack, but I chiefly desire to call your attention to this type of kiln, whether the stack be nside or outside. For many purposes I prefer the center

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stack and in other cases we could find just as good reasons for an outside stack serving two kilns.

This type of kiln, however, with a center stack, is a compact, self-contained unit; its floor is on a level with the kiln shed floor which makes it an easy kiln to place; a

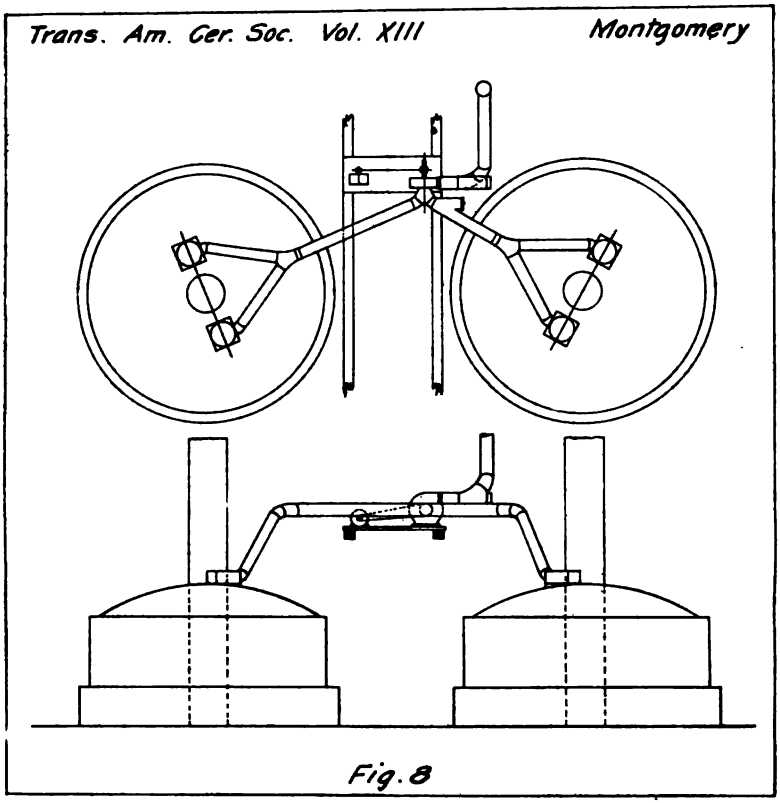

Fig. 8

careful regulation of the floor openings will give perfect distribution of heat from the outside ring to the center; and given careful firing and sufficient time, it will give even heat from top to bottom. The stack heats up rapidly, giving a good draught almost at once after starting the fires. It also forms a support for the ware or the bungs, and is of considerable advantage in many cases, especially

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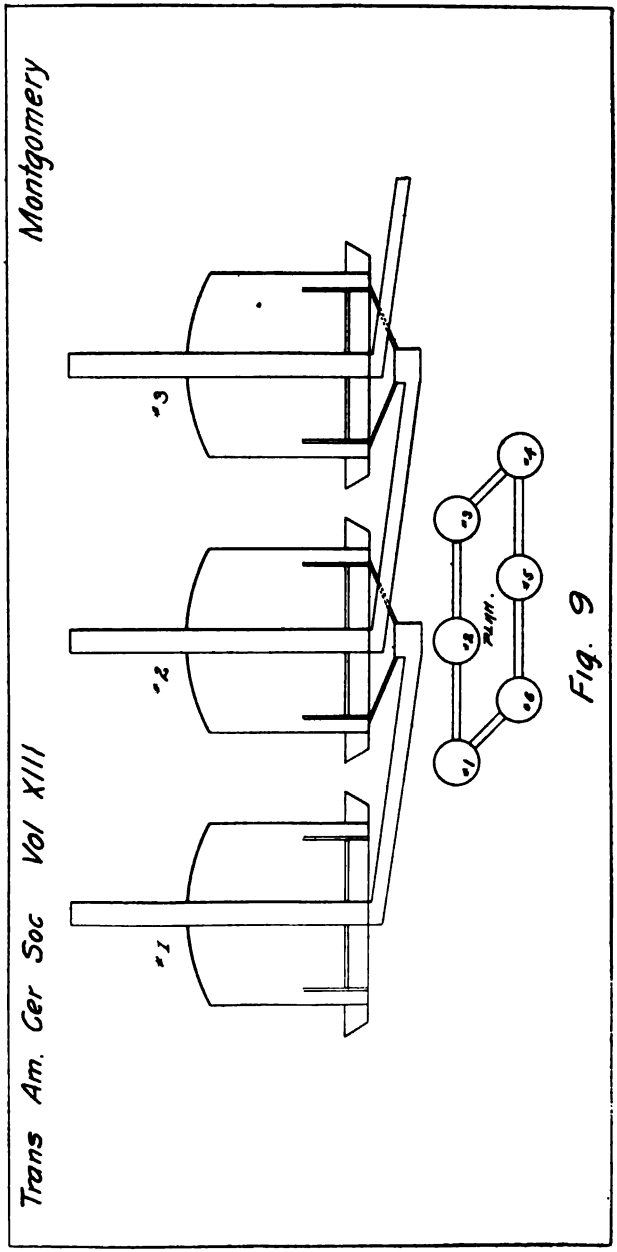

Fig. 9

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at high temperatures such as those used in the porcelain industry. It is adapted to the waste heat drying system by the use of the crown plugs shown and an exhaust fan to drive the hot air into the drier.

Fuel Consumption.—It is economical in the use of fuel and could be made more so by the application of a continuous system of firing. The kiln described burned an average of 125 bungs of porcelain to cone 11 down, 12 started, in 36 to 40 hours, using an average of 9 tons of good bituminous coal.

Continuous System.—The center stack also lends itself to the application of the continuous principle much better than the same kiln with an outside stack could do. An idea of such a system is given in the following sketch: After kiln No. 1 is started through its own stack, the damper is closed and it is forced to draw through No. 2 and its stack, the hot gases from No. 1 being introduced at the bags in No. 2, possibly through a hollow bag wall or, better, through the kiln walls by means of flues and into the bags above the fire. The gases would be too hot to introduce under the grates. When No. 1 is finished and the fires are started on No. 2, it would in turn discharge its heat into No. 3 and so on around the circle, thus saving a great deal of the heat carried out in the waste gases where each kiln is fired separately.

In closing, I wish to say that I trust this paper may serve the good purpose of bringing into our "Trade Journals" and into the "Transactions" of our ceramic societies and associations, the exact descriptions of many other types of kilns of good construction and of proven worth, which are in daily use in the many different branches of the industry.

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EXPERIMENTS ON FRITTED ENAMEL GLAZES AT CONE 1-3.

By FREDERICK RHEAD, St. Louis, Mo.

These experiments were based on a chrome-tin-pink fritt, the formula of which had been given me by Mr. Morton, of the Mosaic Tile Co., Zanesville, O. His formula was:

White lead	57.0
Feldspar	89.0
Whiting	65.0
Borax	12.0
Flint	72.0
Boracic acid	51.0
Oxide of tin	27.0
Carbonate of soda	2.0
Oxide of chrome	0.25

When melting as a drop fritt in a Caulkins fritt kiln, it was a green glass and quite fluid.

I ground the fritts until they readily passed an 80-mesh sieve, then added gum of tragacanth, and applied them with a brush.

When fired in a Caulkins muffle kiln at cone 1 down, the red was lighter than the original sample given to me by Mr. Morton and had cloud-like white segregations throughout, resembling somewhat some of the English majolica glaze effect.

I also tried this same base fritt without the chromium, but using other oxides fritted in as follows:

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Material	Morton's glaze	Glaze 21	Fritt 23	Glaze 73	74	75	76	78	79	80	83	81	96	97	98	99	100
Oxide chromium	¼					10											
Potassium bichromate		¼															
Sodium nitrate		2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
ZnO			10	10			10	10									10
Black oxide copper				6				2					4	3	2	1	2
Black oxide cobalt			½			1		½		½							1
Yellow uranium							9										
Japanese Red											10						
Black oxide manganese												6					

In the following glazes the stain was added to the ground fritt:

Material	Glaze A	B	C	D	E	F	G	H	I	J	M	L	M	N	O
Glaze 74	100		100		100		100			100		100	100	100	100
Uranium nitrate	5	5													
Glaze 99		100		100		100		100	100		100				
Nickel nitrate			5	5											
Cobalt nitrate					5	5									
Silver nitrate							10	10							
Copper sulphate									5						
Oxide of chrome										5	5				
Chrome alumina												5			
Ferric chloride													5		
Japanese red														10	5

We obtained colors and freak effects with these glazes that were superb. As glazes for majolica art ware, they give promise of being not only unique in effect but such as would find favor.

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METHODS EMPLOYED IN CONNECTION WITH THE REDUCTION, MILLING AND SHIPMENT OF QUARTZ, FLINT ROCK OR SILICA SAND.

By HARRY F. SPEIR, Lewistown, Pa.

INTRODUCTION.

Quartz is the general term for crystalline silica whether it be sand or boulder. Flint applies strictly only to amorphous, *i. e.*, non-crystalline form of silica. Flint has a dull surface and is frequently of rounded form. Both may be pure silica.

Many of the smaller and nearly spherical flints imported from France or Denmark are found in the chalky deposits along the coast and are used as balls in tube mills. Their consumption in this connection is very large in the cement industry, and, after being calcined and ground, are used in the pottery and kindred trades. These flints, which are usually gray to nearly black in their natural condition, become perfectly white after burning, and are easily fractured.

The amount of pulverized rock flint, or quartz, consumed in this country in 1908 was, approximately, 20,000 tons, as against almost three times as much pulverized silica sand consumed during the same period. Each year shows a decrease in the proportional amount of pulverized flint consumed, pulverized silica sand being used instead. The sand has been found to give satisfactory results, and can be manufactured and sold at a much lower cost.

METHODS OF REDUCTION.

There are two methods of pulverizing the potter's "flint," one known as the wet process, which was the original method, the second the dry process, which is less expensive and now more generally practiced. In the wet process, the quartz boulders are usually burned in kilns and then fractured. The first crushing is either through jaw crushers or in chaser mills. After reducing the mate-

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rial to about what would pass through a No. 8 mesh screen, it is ground in wet pans. These so-called pans are usually made of cypress wood, being 10 1/2 feet in diameter and 2 1/2 feet high. Each has a pavement of flat faced quartz about 12 inches thick. There are four revolving arms attached to a central upright shaft making about 9 R. P. M. The runners or grinders are heavy quartz boulders, measuring approximately 15 inches square. Two or three of these boulders are placed in front of each of the revolving arms. The crushed quartz, after being placed in these pans together with a quantity of water, is pulverized between the revolving boulders and the pavement.

In order to reduce the material to the required fineness (approximately 120 mesh) usually about 24 hours of continuous grinding is necessary. The amount of material ground varies with the size of the pan, but is usually about 1200 to 1500 pounds per charge.

After the required grinding, the contents of the wet pans, which become rather a pastelike mass of pulverized quartz and water, are passed over a wire screen into a series of settling troughs. That which accumulates in the first trough, being the coarsest, is usually returned for further grinding. The length of time the material is permitted to remain in these troughs depends upon its fineness and the time required for the pulverized material to settle. Where a number of troughs are installed, several different degrees of fineness are obtained, the accumulation in the first trough being the coarsest and in the last trough the finest, with sometimes one or more different grades between, each grade being kept separate during the balance of the process.

After the water is drawn off (the flint having settled to the bottom of the troughs), it is shoveled out and spread upon drying floors, or is placed on top of long low kilns heated by burning logs, or it is put into small pans which are placed tier on tier on heated racks constructed of steam pipe.

After the material is dried, it is sometimes bolted

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through revolving wheels covered with brass cloth of such mesh as will insure the required degree of fineness, and then packed into bags or barrels for shipment, or else shipped in bulk, according to trade requirements.

In some few instances, the product is thoroughly dry when shipped, but usually it contains about 10 per cent. of moisture.

Dry grinding is far less expensive. If used at all, the method of burning and crushing the flint is identical with that employed in the wet system. The dry process is either intermittent, having small pebble mills, usually 6 by 8 feet; or continuous (which is the most modern), using tube mills, or cylinders, usually 6 feet in diameter, 24 feet long. These mills, constructed of either iron or steel, in either system, are usually lined with either porcelain blocks or Belgium silica stone, the former being manufactured, the latter being quarried in Belgium and imported. The silica stone has been found to be less expensive, to posses a much longer life, and also to be better suited for this purpose.

The Intermittent Process.—Where the small intermittent pebble mill of the size mentioned is employed, it is usually customary to carry approximately 1 1/4 tons of flint pebbles and 1 ton of silica sand, or finely crushed quartz, in each mill. After these mills are so charged, they are permitted to revolve, usually for a period of from 6 to 8 hours, depending upon the fineness required, the rolling action of the flint pebbles reducing the sand or finely crushed quartz to a powder. The solid man-head, or door, is then removed and replaced by a perforated man-head. The mill is then permitted to revolve for a short period, the pulverized material passing through the perforated door and the flint pebbles being retained.

There is some objection to this method, because it permits small pieces of flint pebbles and other impurities to be discharged with the pulverized product, which receives no further screening, being generally discharged into large bins where it is dampened with water and loaded into

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wagons for local delivery or else loaded into box cars for shipment. Usually one man superintends the operation of five pebble mills of this character, whose duty it is to test a sample of the product of each mill for fineness before it is discharged. There is some question as to whether material of this character can be satisfactorily ground by this method, because either flint or sand will vary in its degree of hardness, hence six hours' grinding with this process may produce a certain result one day, and entirely different result the next day.

After these closed mills are put into operation, the miller, or man in charge, has absolutely no control over the grinding which is taking place within. He cannot (while the mills are in operation) cause them to grind finer, except by keeping them in operation for a longer period. He does not know what result is being obtained until the mill is stopped and its contents examined. The flour miller, with his old Buhr stone system, or more modern steel rolls, always sees what his mills are producing, as is also the case with the continuous feed and discharge system to be described, and in these instances the grinding can be easily regulated and controlled. This is a very important feature.

The Continuous Process.—The continuous method of milling is, in my judgment, far superior to the intermittent method. It has been adopted by the cement industry without exception. I will describe this method as it is employed at the plants with which I am connected.

The sand is mined close to the works, thoroughly disintegrated and cleansed by washing. It is then thoroughly dried and screened through revolving screens to eliminate any pieces of sticks or foreign matter which may have been mixed with it. It is then conveyed to the pulverizing department, where it is fed automatically into the continuous tube mills.

These tube mills are lined with Belgium blocks and each mill carries approximately 10 tons of the flint pebbles as grinders, and 5 tons of the thoroughly washed and

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dried silica sand. The coarse sand is continually flowing into the feed end, the finished product being discharged at the other end, passing through a perforated plate which prevents the pebbles from leaving the cylinder. It is then passed through a revolving screen to eliminate any foreign matter. The quantity produced per minute and the fineness of the product depend upon the quantity fed.

These mills are operated in series, that is, two of these large tube mills are employed, one being known as the "breaker" and the other as the "finisher." The coarse sand enters the breaker mill and is pulverized to about an 80-mesh, then discharged into the finishing mill which reduces it to the required fineness. By employing this method, it has been found that uniformity of grinding is invariably obtained.

By feeding the sand to the mills more rapidly, a coarser grade is produced, and *vice versa*.

The material being discharged is tested every half hour to insure proper grinding.

The grinding of about 35 tons of sand will, by this method, consume about 100 pounds of flint pebbles. Additional pebbles are frequently added to replace those which have been reduced to a powder, it being necessary that these pebbles be kept to a certain height in the tube mills to insure the best results.

Each mill has its individual motor drive to prevent variation in speed during operations.

When the finished product is to be shipped in bulk, it is loaded into box cars automatically. In fact, for bulk shipments, after entering the pulverizing department no human hand comes into contact with it, except to test the material periodically as before described. The automatic feeding device permits the miller to know the quantity of material he is producing per minute and by this method he regulates the loading of cars to the required tonnage.

When shipped in bags, the material is discharged from the mills, passed through the revolving screen directly into bags underneath which are platform scales. The

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arrangement permits of two bags always being in place. The scales are set for 102 pounds. When a bag has the required weight and is being tied and removed, the second bag is being filled and a new bag replaces the first one, and so on. The mills are so arranged that, if occasion requires, either mill of a series can be operated as breaker or finisher.

DISCUSSION.

Mr. Watts: I am inclined to believe that calcining of flint has a marked influence on the action of that flint in the body in which it is used. To what extent that action may be important, I cannot say; but we do know that the difficulties that arise from flint that is unfired do not arise from flint that is fired.

I believe that the gradations in the flint, and the amount of very fine material as related to the amount of coarser material, have an important bearing on the working properties of flint or the success with which it is used in a body. I do not believe that any one will contradict me when I say that the wet-ground flint from England produces results that you cannot get from the dry-ground American flint. No one claims that dry-ground flint is a superior product, and none of the latter can be ground by any reasonable process to the degree of fineness that can be obtained by the wet-grinding process.

Mr. Speir: A number of years ago before undertaking to pulverize sand, I came into Trenton and spoke to a number of prominent potters. They all said that pulverized sand could not be used for pottery ware, but that they must have rock flint for that purpose. To-day 4/5 of the so-called pulverized flint used in this country is pulverized silica sand, dry-ground. That shows that the potter has adapted himself to this material, because it was evidently to his interest to do so. Recently, one of the foremost potters in this country has come to us unsolicited and asked us to send him one hundred pounds of pulverized silica sand, because he thought, from some previous small experiments,

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he could use our material, and he considered it to his advantage to do so.

Mr. Watts: A certain gradation of flint must exist in order that the flint shall do its proper work. When we talk of one hundred-, of one hundred and twenty-, or one hundred and fifty-mesh flint, that is not the whole story; the proportions of the one thousand-mesh, the two thousand-, the five thousand-, and perhaps the ten thousand-mesh flint are equally important. As graded size of stone or gravel produce the best concrete, so graded size of ground flint produces the best pottery. The German potter considers that very fine-ground flint is extremely important. Incidentally, he does not use so much flint as some American potters, in proportion to the amount of clay.

Mr. Stover: Have you ever seen one of these continuous tube mills tried with a wet process?

Mr. Speir: These mills are used in that manner in the West, in the gold districts; and they can pulverize more material in a given length of time than is produced by the dry process. Only forty-four horse-power is consumed by one continuous cylinder, size 24 feet by 6 feet, in the wet process, as against 86 horse-power with the same character of mill operating on the dry process. While you grind more material and save considerable power (which is a very serious item in this business), yet the feature of handling the material after it has been ground, and the drying of it, necessitates such a severe expenditure as to make it unadvisable for us to use the wet process. The potter will not pay the price proportionate to the cost of producing wet-ground flint. He says that the dry-ground material is satisfactory and he does not want to pay any more for it.

Mr. Stover: You made one statement about getting one grade of fineness one day, and another grade the next. Now what the potter wants is to get what he orders continually and without variations. In some work that I was carrying on, we got a certain series of results one time, and another series at another. We thought that we had

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the same material both times, but we had not. It was not from your mill. I attributed this result to some of the ground material, and had it separated into coarse, medium, and fine. I then started again, with a certain amount of each. After this, I was able to duplicate my results. If we had different proportions each time, there would be difficulty.

Mr. Speir: Yes, the wet system will grind flint more uniformly than will the dry; and when the potter guarantees to us that he will make it to our interest to adopt such a system in a separate mill for his purposes, we will do it.

Mr. Binns: There are two points that mainly press upon us. One is the question of wet *versus* dry grinding and the other is the possible result in the nature of grading the sizes of flint. I believe, personally, that the wet-grinding process, particularly in the drag-mill, is more effective in giving us that packing of sizes to which Mr. Watts has alluded; and I am rather firmly convinced that this is what we need.

Mr. Speir quoted a remark to the effect that if flint is too fine, it will cause cracking; and that if it is too coarse, it will cause crazing. That remark occurred in a paper read by Mr. Ashley last year, I think, and it was criticized by some of the members. It is perfectly true that a too fine flint will cause ware to crack, because it makes the clay so dense that water cannot escape on drying. A good many persons have been deceived by this phenomenon. Of course, fine flint makes finer ware; and, from the point of view of those making fine china, you cannot have the flint too fine. On the other hand, from the manufacturer's point of view, when you make wares at great speed, you reach the margin of safety beyond which the clay will crack in the mould as it dries.

Mr. Ashley also made the statement that the coarser the flint was, the stronger would be the ware. That is true; but the coarser the flint, the worse the pottery is apt to craze when burned. The two things have to be

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compromised. The true condition in which our materials should be is that illustrated by Mr. Watts. They should pack together. We should have a definite proportion of flint of different fineness, so that one kind of grain may fit into the interstices left by others.

The next question arising is: "Does the wet process or the dry process produce this condition in the best way?" Here we have the view that neither the one nor the other does, but that the method of grinding the flint is responsible. All the modern works that I can see, however, are in favor of the older method; and I am inclined to think that the grade of flint produced by the old-fashioned drag-mill is the best grade for the potter's purpose.

Mr. Speir: Have you ever tested the pulverized material produced in a ball-mill as compared with that produced in the drag-mill?

Mr. Binns: Yes, I think that I am familiar with the material in every condition. I have made a number of experiments, and have followed the progress of the ball-mill very carefully. I have not known of the use of continuous tube-mill for grinding of flint until to-day. I am glad that it has been applied to this purpose, but I am not prepared to admit that it is superior, except in cleanliness. I do not think that the grade of flint produced by it is more suitable than is other material. I believe that it is too uniform, and that is not what the potter wants. I hope that one of those who are practiced in the more delicate manipulation of materials and have more facilities at their disposal, than I have, will plot for us an ideal curve that will give a certain proportion of flint of different grades fitting together mathematically. I think that it is possible to do this, and should like to see it done. Then, I think, we can reach a more definite conclusion regarding the matter.

Mr. Speir: I do not know whether you are aware of the fact that wet-ground flint can be obtained in this country, but that there is less and less of it being bought by the potters, because of its price. Wet-ground flint may make

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better ware, but it apparently does not make it sufficiently better to offset the difference in its cost as compared with the cost of dry-ground flint. All your theory notwithstanding, what the manufacturing potter actually does in this matter is to make a practical test for "The proof of the pudding is in the eating." The potter has used wet-ground flint, and is now using the dry-ground. Why? It may not aid him in producing a better piece of ware, but it is evidently to his interest to use it, otherwise why is he doing so, and why is the demand for dry-ground silica sand increasing? The price is a very important consideration when making ware commercially.

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THE CHEMICAL AND PHYSICAL PROCESSES INVOLVED IN THE FORMATION OF RESIDUAL CLAY.

By H. O. BUCKMAN, Ithaca, N. Y.

A study of the processes of residual clay formation necessarily involves a discussion of the work of weathering agents. The intensity and period of action of these agents, whether physical or chemical, determine the degree to which a rock is disintegrated or decomposed. To rightly understand the physical and chemical characteristics of clays and, indirectly, their consequent utility, a clear comprehension of the steps by which they were formed is of considerable importance.

Clay is a product of rock destrucion by weathering agents. These agencies are grouped under two general heads, mechanical and chemical. To clearly and quickly explain the character of the forces at work in their logical relationships, the following outline is given:

General Weathering.

I. Mechanical Changes or Disintegration.
   - A. Erosion and Denudation.
     Water, Ice and Wind.
   - B. Temperature.
     Frost, Heat and Cold.
   - C. Plants and Animals.

II. Chemical Changes or Decomposition.
   - A. Oxidation.
   - B. Hydration.
   - C. Solution.
     Water, Pure or Acidulated.
   - D. Deoxidation.

Pure clay or kaolinite is a hydrous aluminium silicate and results primarily from the decomposition of feldspars. These minerals, under processes of weathering, lose more or less completely their soluble constituents, the alkalies, alkaline earths and iron. This leaves behind a residue of

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alumina and silica whose purity depends on the character of the weathering, and the composition and texture of the parent rock. Obviously, then, the process of disintegration is a factor in this discussion only so far as it aids in disrupting the rock and facilitates the chemical changes. Of the mechanical agencies already enumerated, water is of primary importance. Its presence in the rock interstices makes frost a force capable of splitting the strongest stones. Extreme changes of temperature, whether in a dry or moist climate, exert untold power in splitting, exfoliating and chipping rock surfaces. Wind, armed with sand, becomes an eroding force in dry arid lands but as a general rule its effect is but slight. Plants and animals, while of small importance perhaps in the actual processes of fining rock materials, are of inestimable importance in the formation of a fertile soil.

Interested as we are in the more closely related processes of clay formation, we may pass by the mechanical side of rock decay with these few observations and take up more in detail the chemical aspects of the subject. However, we must not forget, as pointed out above, that disintegration opens a pathway for decomposition, since the fining of rock, by mechanical forces, presents a greater surface to chemical attack. Moreover, the forces of disintegration vary so greatly with the texture, composition and position of rocks, and also with the climate, altitude and vegetation, that a detailed discussion of each would be necessary to completely cover the field.

It is important to state, however, that disintegration continues to occur with more or less intensity long after the rock mass has been reduced to a fine state. In fact, disintegration and decomposition work together so closely that it is impossible to separate their actions even after the weathering material is in a state to permit of fairly rapid chemical decay.

Chemical Decomposition of Rocks.—The processes of rock decomposition are grouped under four heads, oxidation, hydration, solution and deoxidation. Each group

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represents a single operation but becomes more and more complex as the end products are approached. The dissolving out of minerals as a rock decays is in itself a complicated problem but with this there is always oxidation, hydration and, usually, disintegration. It is seldom that one force acts alone and where the rock is exposed, they all operate in the tearing down of the existing aggregate and the building up of more stable compounds. Indeed, the complexity of the phenomena of weathering is such that exact rules will not apply.

Decomposition of rocks, in general terms, means an assumption of water, oxidation of iron and a loss of soluble bases in the form of carbonates or bicarbonates. Under such conditions, then, a chemical analysis must be interpretated with caution. Especially is this true in ascertaining the probable composition of the original rock. In a study of the origin of clays, the chemical components present in the parent rock must first be considered. A proper solution of the question lies in working from the rock-type to the clay-type.

Moreover, the decomposition of rocks can be understood only by a knowledge of the composition of its constituent minerals. If this can be carried one step farther and the chemical decay of the minerals studied separately, the changes which occur in the rock can be forecast with considerable certainty. The minerals, each having different textures, crystalline structures, physical properties and chemical composition, determine the stability of the rock. The problem then is to obtain the relative resistance of each mineral and apply this factor to our study of the rock. Such data can be used to explain the chemical changes shown by the analyses of fresh rocks and their residual clays.

Solubility of Minerals.—Considerable work has been done on the comparative solubility of minerals although in most cases it is quite inconclusive. This is because it is sometimes difficult to duplicate natural conditions experimentally. The mineral must be powdered extremely

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fine in order to make action rapid enough for observation and reduce conditions to a point where the results can be considered as comparable. The best investigations have been carried out with feldspars, probably because this mineral is so common and of such importance as a constituent of many rocks and as a clay builder.

Among the first to do work along this line were W. B. and R. E. Rogers (119*a*),[1] of England, who, as early as 1848, established the fact that pure as well as carbonated water acted upon rocks. However, they carried the investigation no farther. Headen (63*a*) was able to obtain some interesting data upon the solubilities of feldspar by placing the powdered mineral in a gallon aspirator and treating it with distilled water in four eight-hour periods. The rock was agitated by a current of carbonated air. When thirty-five gallons of solution were obtained, the water was evaporated and the residue analyzed.

In a second experiment, the powdered rock was merely allowed to stand for 22 days in water saturated with carbon dioxid, the mixture being subjected to frequent shakings. When the bottle was opened, air was passed through the water and the soluble iron precipitated. The residues were analyzed as in the first experiment. The following table gives the composition of I, the fresh feldspar; II, the residue from the first experiment; and, III, the residue from the second experiment.

	I	II	III
SiO_2	65.76	40.72	14.35
Al_2O_3	19.29	2.70	1.11
Fe_2O_3	trace	0.31	0.13
CaO	0.31	10.24	23.41
MgO	0.02	0.77	1.19
K_2O	11.59	10.97	11.27
Na_2O	2.72	5.24	6.49

[1] The numbers in parenthesis refer to the papers listed in the bibliography at the end of this paper.

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The precipitation of the iron was unfortunate because no data could be obtained regarding its solubility as ferrous oxide. This is important as the iron in the ferrous state is quite soluble and has much to do in the breaking down of rocks. However, it quickly changes to the ferric iron, and is one of the least lost elements when subjected to the action of water. In the ferrous state it is one of the most unstable oxides, while as the ferric oxide it rivals alumina in its small loss in chemical decomposition.

From the above analyses the following ratio of per cents.[1] can be calculated, showing the relative solubility of the constituents.

	1st residue	2nd residue
Al_2O_3	0.139	0.057
SiO_2	0.619	0.218
K_2O	0.952	0.990
Na_2O	1.926	2.380
CaO	3.303	7.550
MgO	38.500	59.500

One especially noticeable feature is the increased solubility of the sodium, calcium and magnesium when exposed to the action of carbonated water. Again, these figures show the low solubility of alumina and silica, and the higher relative solubility of potash, sodium and calcium. As any one of these is many times more soluble than the alumina and silica, their resistance must mark the general resistance of the feldspars to solution. This being the case, the feldspars, in regard to their solubility, would be arranged with the potash feldspar as the least soluble followed by the soda, soda-lime, lime-soda and lime feldspars, respectively.

In 1877, Müller (101*a*), submitted certain minerals to carbonated water in order to determine their order of

[1] This ratio is obtained by dividing the percentage of any constituent in the residue by its percentage in the fresh rock.

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solubility. He found that they stood as follows: orthoclase, oligoclase, serpentine, hornblende, apatite and olivine. Expressed in percentage loss of each constituent, his findings were as follows:

Adularia...	SiO_2 0.155	Al_2O_3 0.137	K_2O 1.353	
Oligoclase..	Al_2O 0.171	SiO_2 0.237	Na_2O 1.367	K_2O 3.213
Hornblende	SiO_2 0.491	FeO 4.829	K_2O 8.528	
Augite.....	FeO 0.942			
Magnetite..	FeO 2.428			
Apatite....	CaO 1.696	P_2O_5 1.417		
Apatite....	CaO 2.168	P_2O_5 1.822		
Apatite....	CaO 1.946	P_2O_5 2.120		
Olivine....	SiO_2 0.873	MgO 1.291	FeO 8.733	

Alexander Johnstone (77*a*, *b*, *c*) also treated certain powdered minerals, for a year, with carbonated water, with the following results:

1. With feldspars, orthoclase was most resistant and labradorite least.

2. Hornblende and augite were acted on more rapidly than were even the most soluble feldspars.

3. Biotite lost MgO and FeO in the treatment.

4. Muscovite was the most resistant of minerals tested.

5. Olivine was but slightly attacked by carbonated water.

This confirms Müller's work except in the case of olivine. Just why Johnstone made this finding on a mineral so readily soluble is difficult to explain.

However, Cushman (28*c*), in a careful work upon rock-powders, found that with wet grinding a colloidal substance was formed about the particles. This material, consisting of siliceous matter and aluminium silicates, had the power of absorbing salts in different amounts under different conditions. Weighed portions of the rock were treated and digested with various electrolytes (NH_4Cl, $BaCl_2$ and $Al_2(SO_4)_3$). Bases were absorbed quickly, the amounts varying with the time of digestion. In rock

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residues, then, the potash, as well as other salts, may be held by the colloidal material and but little set free.

This investigation throws some doubt, not upon the reliability of the work already done, but upon the interpretation of the results. However, Clarke (23*b*), after a careful summary of the literature on rock solubility, including Cushman's work in wet grinding, seems inclined to receive the work of Müller and Johnstone as indicative of the true condition. He makes a broader classification of the minerals in the order of their least solubility.

Primary	Secondary
Quartz	Corundum
Muscovite	Zircon
Biotite	Magnetite
Orthoclase	Apatite
Plagioclase	Pyrite
Pyroxene	
Amphibole	
Olivine	

Clarke (23*a*), using phenolphthalein as an indicator, came to the same general conclusion although the methods used were not calculated to give specific results. He found that muscovite was more resistant than biotite and that orthoclase was less soluble than plagioclase. Van Hise[1] considers that we should expect the heavy alkaline minerals to decompose first, then the alkaline earth minerals, followed by the ferro-magnesium and, lastly, by the aluminates. This would imply a classification of nepheline, leucite, olivine, pyroxene, amphibole, feldspar, biotite and muscovite. He also states that of all the chemical constituents, aluminum oxide is the most resistant to solution.

Merrill,[2] in his résumé on rock weathering, states

[1] Treatise on Metamorphism, U. S. Geol. Surv., Mono. XLVII, p. 518.
[2] Rocks, Rock Weathering and Soils, p. 220, New York, 1906.

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that free quartz is barely soluble at all but that most of the silica found in solution comes from the breaking down of the silicates. This is, in general, quite true, although Hayes (62*a*, *b*) in an investigation of the conglomerates of Virginia and Tennessee found that humic acids had the power to corrode and dissolve quartz pebbles to a marked extent. Sorby[1] also makes a record of similar observations in England. Of the silicates, those containing the protoxides of iron with magnesium or calcium are most readily decomposed. This means, then, that the silicates of aluminum are less liable to decay than those carrying iron or calcium. Becker (7*a*), in his report on rock decay in the Comstock Lode of Nevada, notes the same phenomena, namely, that feldspars were more resistant than augite and hornblende. Dana[2] found that olivine in basalts gave away long before the augite in the same rock, while Roth[3] observes that potash was always conserved to a larger degree than soda. Merrill[4] also found that muscovite was invariably bright and intact when the biotite was in an advanced stage of decomposition. He further states that potash feldspars decompose less readily than those carrying soda or lime.

Daubree (33*b*), in an excellent investigation with orthoclase, determined the per cent. of K_2O soluble in water. Five kilograms of the powdered mineral, after 192 hours of agitation in a cylinder with water, showed 12.6 grams of K_2O extracted. With carbonated water, 2 kilograms of orthoclase, after 10 days' agitation, yielded 0.75 gram of free silica and 0.27 gram of K_2O.

Hoffmann (70*a*), in 1882, allowed water to percolate through powdered mineral for two months and measured the loss in weight. He obtained the following results:

[1] Proc. Geol. Soc., London, 1879.
[2] Report Wilkes's Exploring Expedition, Geology, p. 578.
[3] Allegemeine u. Chem. Geol., 3rd edit., 2nd Heft.
[4] Rocks, Rock Weathering and Soils, p. 220.

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Vesuvianite	0.064
Epidote	0.052
Olivine	0.078
Chlorite	0.094
Talc	0.105
Muscovite	0.056
Biotite	0.35

However, he failed to consider the possibilities of hydration and may have allowed greater inaccuracies to enter. Too high solubility of the muscovite and talc seems peculiar and probably entitles the work to the little weight accorded it.

After a consideration of such data, contradictory in some cases and incomplete in all, any but general conclusions are hard to draw. However, a number of points are clear from concurrence of observation. All writers and investigators agree that muscovite is more resistant than biotite and that quartz is less soluble than both. In all lists of minerals, feldspars are placed next although they may decompose differently under different conditions. Merrill[1] states that in potash feldspar rocks carrying black mica, the latter is first to give away and will almost wholly disappear. In the work of Headen we have conclusive evidence as to the order of the breaking down of feldspars, depending upon the amount of potash, soda and lime present. With feldspars, at least, we may conclude that the most basic are the least resistant. It also seems to be true, in general, that the more silica and alumina present in a mineral, the greater is its stability. The following plate shows the chemical relationship of the various feldspars and makes this point clear.

Applying these data concerning the solution of the potash, sodium and calcium to the more basic minerals, we can obtain a probable reason for their easy decomposition. This becomes more explainable when we consider that the iron in basic minerals is very soluble, but on ex-

[1] Op. cit., p. 220.

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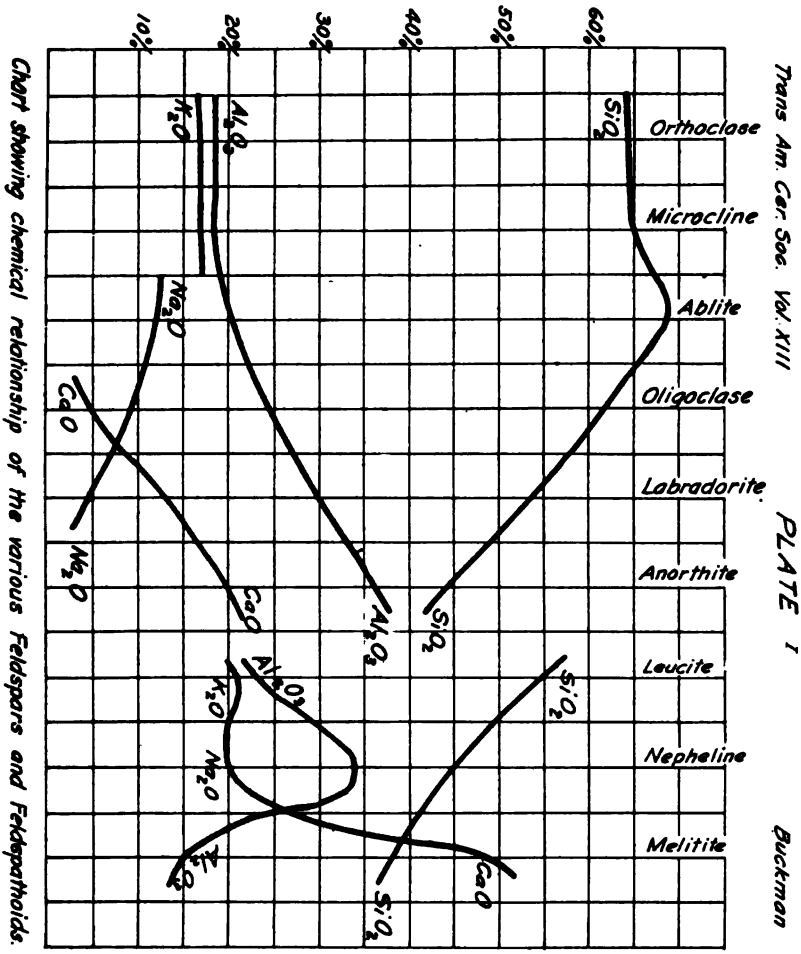
posure to the air is redeposited as the ferric oxide. From the fact that the first indication of weathering is always



shown by iron stains where iron is present, we can, undoubtedly, consider that the iron at least is as easily attacked as the other constituents. Magnesium was shown, by Headen, to be more soluble than calcium.

Comparing, now, the composition of anorthite, horn-

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blende and olivine, we find them to be calcium-aluminum, calcium-iron, or magnesium-iron and magnesium-iron silicates, respectively. Their formulae are:

$CaAl_2Si_2O_8$	Anorthite
$Ca(Mg,Fe)_3(SiO_3)_3$ with $Na_2Al_2(SiO_3)_4$ and $(Mg,Fe)(Al,Fe)_2SiO_6$	Hornblende
$(Mg,Fe)_2.SiO_4$	Olivine

The chemical reason for their different resistance to solution is plainly seen. In the case of feldspar and hornblende, the latter contains no aluminum and proportionally more of the combined calcium-iron or magnesium-iron than the anorthite does of calcium. This condition is more favorable for decomposition. The same is true also of olivine. We may say, then, with regard to these groups of minerals, that the more basic they become, the less their resistance to solution, either to pure or carbonated water. However, a query as to biotite may be made here. It is a highly magnesium mineral, yet it is placed above the feldspars in the classification. No reason is known for this unless it is because of its peculiar structure or water of crystallization.

From this general survey, a classification can be added to the data already cited, which expresses the probable solubility of the minerals when exposed under similar conditions.

1. Quartz
2. Muscovite
3. Biotite
4. Orthoclase
5. Plagioclase
6. Epidote
7. Serpentine
8. Talc
9. Hornblende
10. Augite
11. Apatite
12. Olivine
13. Leucite
14. Nepheline

Calcite, dolomite and gypsum occur in certain stratified rocks on their metamorphosed derivatives and are very soluble. Under any conditions of hydration they

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will go into solution. Epidote is often an alteration product, from ferromagnesium minerals and feldspars and would, therefore, be more stable than the former but less so than the latter. The talc and serpentine, as alteration products of the ferro-magnesium minerals, will in the same way be more resistant.

Decomposition of Rocks.—Turning, now, from the minerals to the rocks themselves, we find a difficult question confronting us. The determination of the solubility of a mineral is comparatively simple, compared to the calculating of the rate of breaking down of a rock composed of different amounts of these same minerals. However, there must be some application of the data heretofore cited, even if only in a general way. That the conclusions must be generalized is evident from the fact that rocks differ so greatly in texture, mineral constituents and chemical composition. The factors are too numerous and varied to allow of specific statements which cannot be verified by direct evidence.

We can make the statement that as we progress among igneous rocks from granite to peridotite, the silica, alumina and alkalies steadily decrease while the calcium and especially the iron and magnesia increase. This means a loss of alkali-aluminum silicates and an increase of iron and magnesium silicates, which we know are less resistant. In other words, quartz lessens and disappears, orthoclase is replaced by plagioclase and this, in turn, is replaced by a pyroxene. Olivine appears in considerable quantities as we pass from acid to basic rocks. With a condition then of a constant lessening of the most resistant minerals and a replacement of these by those less resistant, the relative rate of decomposition of igneous rocks is not hard to formu ate. In short, the more basic an igneous rock becomes, the texture remaining constant, the less able it will be to resist weathering.

Among sedimentary rocks no such general statement can be made because this class of rocks, coming as they do from decomposed igneous rocks, are made up in a great measure of material already worked over. However,

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the general principles of mineral solution can be applied to specific rocks with considerable success. In the case of a sandstone, the point of attack will always be in the cement. If it be siliceous, we can expect the rock to be very resistant to solution, but if the cement be ferruginous or calcareous, then the breaking down will be relatively rapid. Among limestones we find quick decomposition, because the calcium carbonate on becoming a bicarbonate is readily soluble. In clay, which has already been subjected to leaching and mechanical degradation, there is a comparatively small amount of soluble matter and such material may lie exposed for years without appreciable change.

Metamorphic rocks may be considered under both of the heads already discussed, although in texture they more closely approach the igneous rocks. Coming, as they do, from either the sedimentary or igneous, their chemical composition varies within wide limits. Gneisses and schists we would expect to break down very much as granites and allied rocks do. Quartzites and slates would vary, however, and like sandstones should be studied carefully as to structure. Indeed, except among rocks of identically the same structure, comparative resistance is hard to calculate. Because of this, the sedimentary rocks are especially hard to classify. Evidently, then, the best method with any rock is to study actual analyses of fresh and decomposed rocks themselves, with the general principles of mineral composition and solution always well in mind.

For this we shall first consider a fresh and decomposed biotite granite of Georgia. The rock was a finely granular aggregate of quartz and feldspar with an abundance of biotite. The analyses are as follows:

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Fresh and Partially Weathered Biotite Granite.[1]

	Fresh rock	Decomposed	Per cent. saved
SiO_2	70.12	69.17	92.20
Al_2O_3	16.08	17.35	100.00
Fe_2O_3	1.32	1.32	93.61
CaO	1.93	1.18	57.28
MgO	0.56	0.42	71.18
Na_2O	4.37	4.01	85.86
K_2O	5.21	4.75	85.27
Ignition	0.41	1.80	409.09

It is evident that the relationship between the analysis of the fresh and decomposed rock means but little except from careful study. This is true because of the fact that some constituents might show exactly the same percentages and yet have been lost in large amounts. To obviate this and make the changes from weathering apparent at a glance, a number of plates have been devised of fresh rocks and their residues. Thus, in Plate 2, which is so clear as to need no explanation, the figures representing the fresh and decomposed rock are almost identical and throw no light upon the real amount of decomposition that has occurred. A glance at the "percentage saved" circle, however, reveals the whole story. In obtaining the "percentage saved" column the percentage of each oxide saved is calculated, based on the original amount of each constituent present.[2] The oxide which has lost least is used as a constant. Obviously, this will be either Al_2O_3 or Fe_2O_3 and in some cases SiO_2. In the case of the analysis cited, it can be seen that the alumina has suffered the least.

[1] T. L. Watson, "Granite and Gneisses of Georgia," Georgia Geol. Survey, Bull. 9a (1902), p. 309.

[2] $\left(A^1 + \frac{C^1 \times A}{C}\right) \times \frac{100}{1}$ = Percentage saved.

C = % of oxide which is taken as constant in fresh rock.
C^1 = % of oxide which is taken as constant in residue.
A = % of any oxide in fresh rock.
A^1 = % of same oxide in residue.

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Van Hise,[1] in discussing this method of calculation, used the following analysis of a phonolite:

Fresh and Decomposed Phonolite.

	Fresh rock	Decomposed rock	Per cent. lost
SiO_2	55.67	55.72	8.54
Al_2O_3	20.64	22.19	1.60
Fe_2O_3	3.14	3.44	0.00
CaO	1.40	1.28	16.34
MgO	0.42	0.44	4.54
K_2O	5.56	6.26	0.00
Na_2O	7.12	2.65	65.99
Ignition	4.33	7.79	165.39

He says, in regard to this rock: "It is clear that even the large losses of elements are too small. For instance, in this phonolite where K_2O is considered fixed, the loss of Al_2O_3 is 1.6 per cent., but if the loss of K_2O is, for instance, 30 per cent.—and it is probably more than this—the loss of Al_2O_3 was more than 30 per cent. But in the case of Na_2O, the loss of which is calculated at 66 per cent., this amount may be considerably too small, but it cannot be more than 100 per cent., hence, the error is much less than in the Al_2O_3 in this case. Where the losses are given as small in the foregoing table, therefore, it is quite probable that the calculated amounts are but a fraction of the real loss, but where the losses are given as large, the errors, while very considerable, are probably not so great proportionally."

A mechanical analysis of the Georgian gneiss, mentioned above, shows that the coarse material was made up of compound particles while the fine was composed of a single mineral. The particles, however, were sharp and angular. The mica showed some oxidation of iron and the feldspars were partially kaolinized.

This freshness suggests mechanical decomposition and

[1] Van Hise, "Treatise on Metamorphism," U. S. Geol. Survey, Mono. XLVII, p. 507, 1904.

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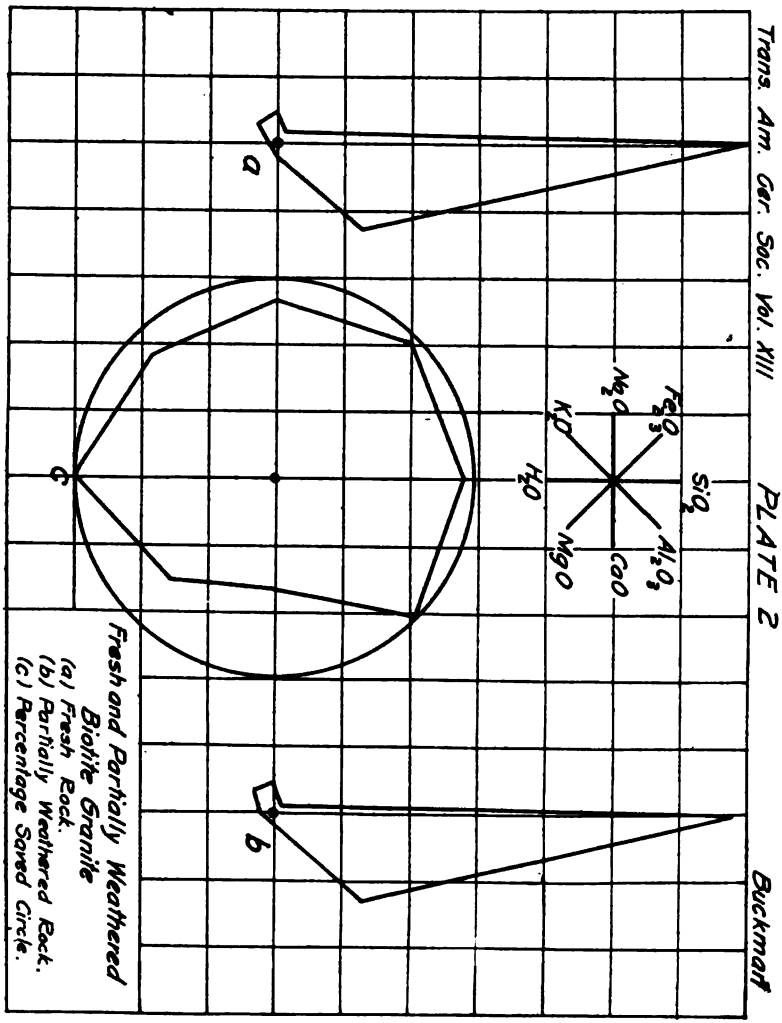
does not at all agree with the general theory of weathering. Such a condition demands a solution of colloidal silica, the



formation of carbonates of sodium, potassium, calcium, magnesium and iron, with later, an oxidation of this iron.

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The feldspars change to kaolinite, the iron becomes limonite and the ferro-magnesium minerals alter to talc and serpentine. A glance at the analyses of this gneiss shows only a taking up of water on decomposition and possibly a change of the ferrous iron to ferric. Plate 2 reveals that the percentages saved of the various oxides almost fills the composition circle. Evidently, then, the rock under consideration has only undergone a preliminary weathering.

A case of complete decomposition is now illustrated in a gneiss from Virginia containing quartz, orthoclase, microcline, oligoclase, biotite and scatterings of apatite and zircon.

Fresh and Weathered Gneiss.[1]

	Fresh	Decomposed	Percentage saved
SiO_2	60.69	45.31	47.55
Al_2O_3	16.89	26.55	100.00
Fe_2O_3	9.06	12.18	85.65
CaO	4.44	...	0.00
MgO	1.06	0.40	25.30
K_2O	4.25	1.10	16.48
Na_2O	2.82	0.22	4.97
P_2O_5	0.25	0.47	106.82
Ignition	0.62	13.75	1285.04

This is a condition of almost complete weathering, the soil consisting of a deep red clay with quartz grains present. It is noticeable that in comparison with the other analysis of gneiss that the loss of almost all constituents is greater. Evidently leaching must have gone on to a large extent carrying the action begun in the former rock nearer to completion. From Plate 3, we can readily see that the figures representing the percentage saved of the constituents has changed markedly from a loss of silica and the more soluble salts, and a relative increase of aluminum and iron. The figures representing the fresh

[1] G. P. Merrill, Bull. Geol. Soc. Amer., Vol. 8 (1879), p. 160.

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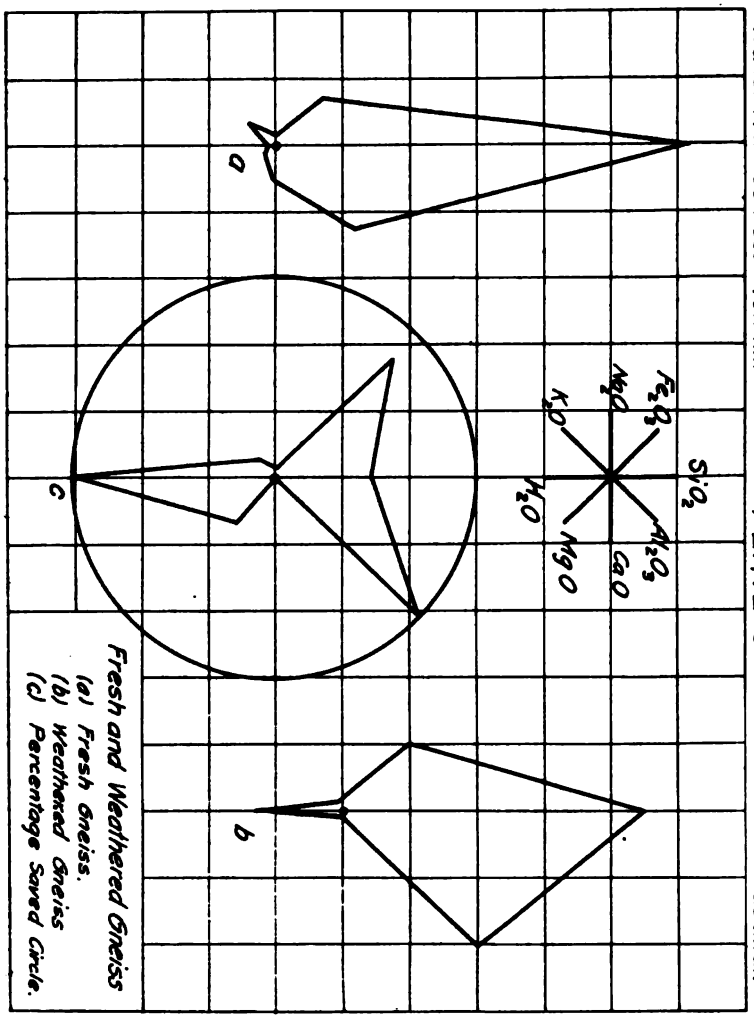
and decomposed rock have not changed very materially however, except from an assumption of water.



In the same way these conditions are illustrated by the analyses of two diabases with their residues. Their

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changes are graphically illustrated by Plates 4 and 5 and serve to further emphasize the points already graphically illustrated.

Medford Diabase.[1]

	Fresh rock	Decomposed rock	Percentage saved
SiO_2	47.01	44.51	81.97
Al_2O_3	20.11	23.24	100.00
Fe_2O_3	3.63	12.71	81.90
FeO	8.83		
CaO	7.06	6.04	74.11
MgO	3.15	2.85	78.30
K_2O	2.14	1.75	70.85
Na_2O	3.91	3.94	87.17
P_2O_5	0.68	0.70	88.61
H_2O	2.71	3.74	120.25

Penokee Diabase and Residual Clay.[2]

	Fresh rock	Decomposed rock	Percentage saved
SiO_2	47.90	41.60	36.43
Al_2O_3	15.60	37.20	100.00
Fe_2O_3	3.69	3.21	36.49
CaO	9.99	0.23	0.96
MgO	8.11	0.02	0.10
K_2O	0.23	...	0.00
Na_2O	2.05	0.07	1.43
H_2O	2.34	13.54	252.14
FeO	8.41	0.30	1.49

As is clearly seen by a comparison of the diagrams of these two rocks, we have a case of partial and complete weathering. In the latter case there is again the marked increase of aluminum and water and a great loss of other constituents, especially the lime, potash, soda and mag-

[1] G. P. Merrill, "Disintegration and Decomposition of Diabase at Medford, Mass.," Bull. Geol. Soc. Amer., Vol. 7 (1896), p. 349.

[2] R. D. Irving and C. R. Van Hise, "The Penokee Iron-bearing Series of Michigan and Wisconsin." U. S. Geol. Survey, Mono. XIX (1892), p. 357.

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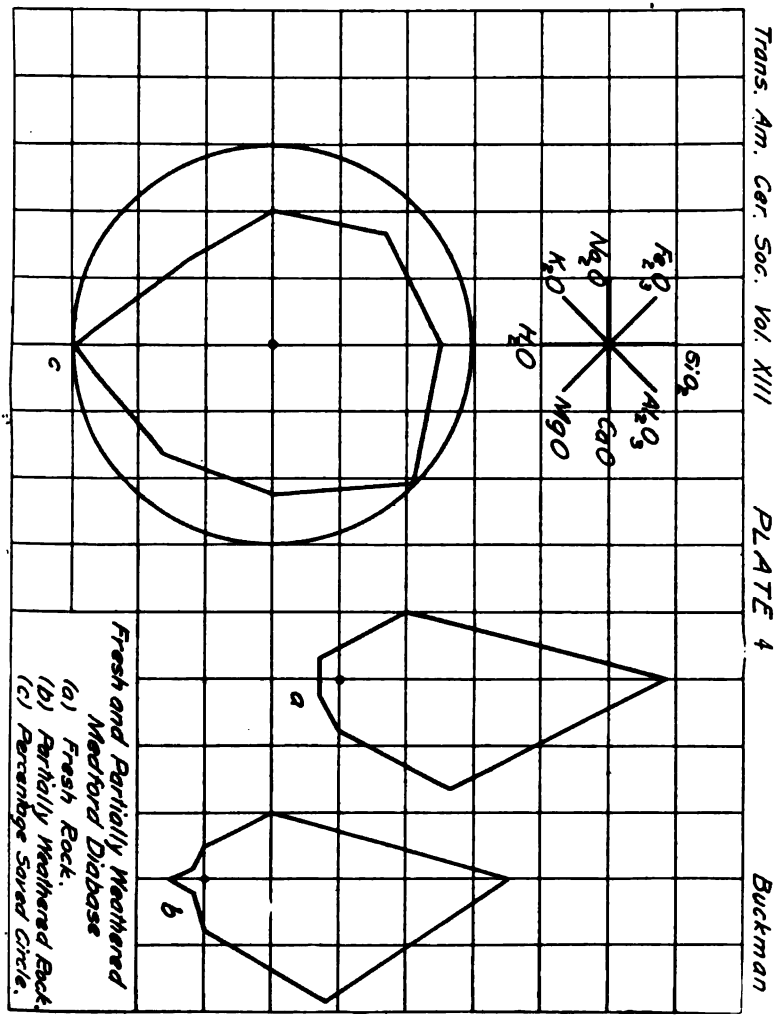
nesium. Again the figures in the percentage saved circle assumes the general form of a three-pointed star, characteristic of completely weathered rocks.



In ordinary limestone, we have a rock which is very easily decomposed, and the solution of one compound

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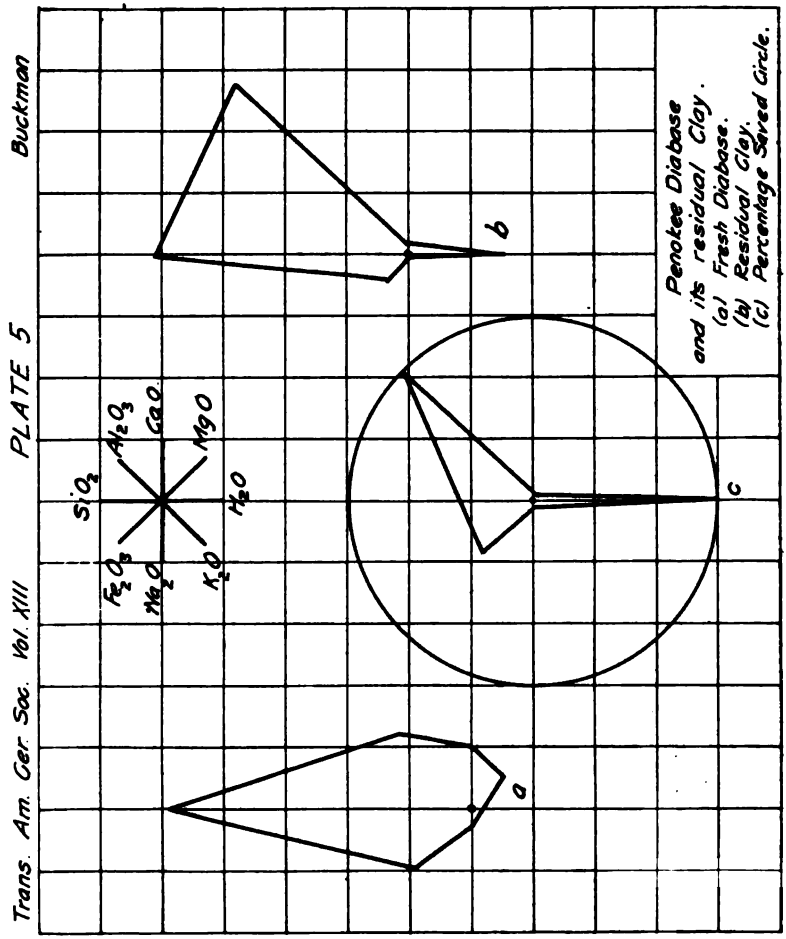
governs the rate of decay of the whole. The action, then, is to a large extent a chemical one. This is markedly



different from the condition found in gneisses and diabases where a certain amount of mechanical disintegration always proceeds and accompanies the chemical action. An analysis of a Virginia limestone and its clay is given

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below as reported in Bull. 150,[1] of the U. S. Geological Survey.

Virginia Limestone and Residual Clay.

	Fresh rock	Decomposed rock	Percentage saved
SiO_2	7.41	57.57	72.61
Al_2O_3	1.91	20.44	100.00
Fe_2O_3	0.98	7.93	75.11
CaO	28.29	0.51	0.17
MgO	18.17	1.21	0.62
H_2O	1.08	4.91	42.51
Na_2O	0.09	0.23	23.96
CO_2	41.57	0.38	0.85
H_2O	0.57	6.69	1096.23
P_2O_5	0.03	0.10	31.22

The result here is a plastic clay made up largely of silica and alumina. 99.83 per cent. of the calcium has been leached away and almost all the carbonate with it. The residue then is much different from the parent rock. This shows a condition entirely distinct from that of gneiss where the clay bears a close chemical composition to that of the fresh rock. It is also noticeable that the water has risen to a thousand per cent., indicating great hydration. Plate 6 brings out these changes in a graphic manner.

In Plate 7 is shown the decomposition of a limestone carrying but a small amount of magnesium. It emphasizes the points already stated and serves to show the general similarity of the decomposition products of limestone. Its analysis is as below:

[1] J. S. Diller, U. S. Geol. Survey, Bull. 150, p. 385, 1898.

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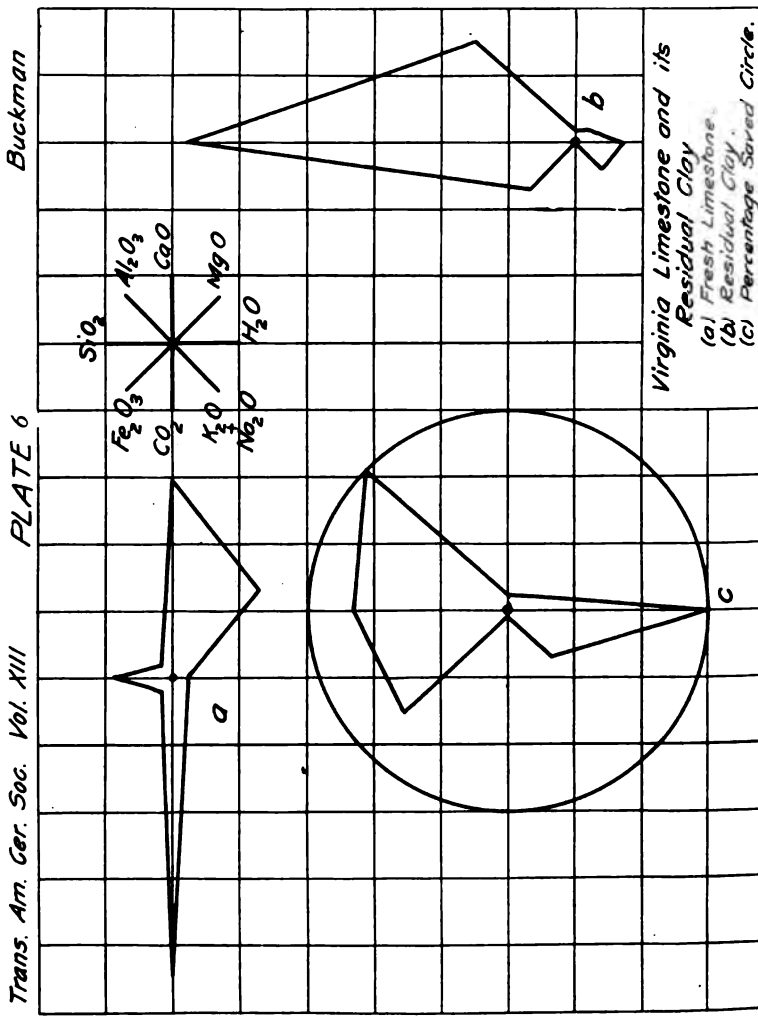

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Arkansas Limestone and Residual Clay.[1]

	Fresh rock	Decomposed rock	Percentage saved
SiO_2	4.13	33.69	100.00
Al_2O_3	4.19	30.30	88.65
Fe_2O_3	2.35	1.99	10.44
MnO	4.33	14.98	42.41
CaO	44.79	3.91	1.07
MgO	0.30	0.26	10.62
K_2O	0.35	0.96	33.63
Na_2O	0.16	0.61	46.74
CO_2	34.10	0.00	0.00
H_2O	2.26	10.76	58.37

It is evident that a large part of this rock has been carried away. Indeed, Whitney[2] estimates that one meter of residual clay in Wisconsin requires from thirty to forty meters of limestone. Russell[3] states that the soil of the Shenandoah Valley, which is a red clay fifty feet thick, has been formed entirely from the impurities of the limestone. Consequently, we may expect the residue of a limestone under most conditions to contain but little carbonate.

It is quite possible, by averaging a number of the rock analyses as to the per cents. of each constituent lost, to determine what ones of the oxides are least soluble. Van Hise has arranged such a table at the close of his

[1] R. A. F. Penrose, Ann. Rept. Geol. Survey of Arkansas (1890), p. 179.
[2] Geol. of Wis., Vol. I (1862), p. 121.
[3] U. S. Geol. Survey, Bull. 52 (1904), p. 24.

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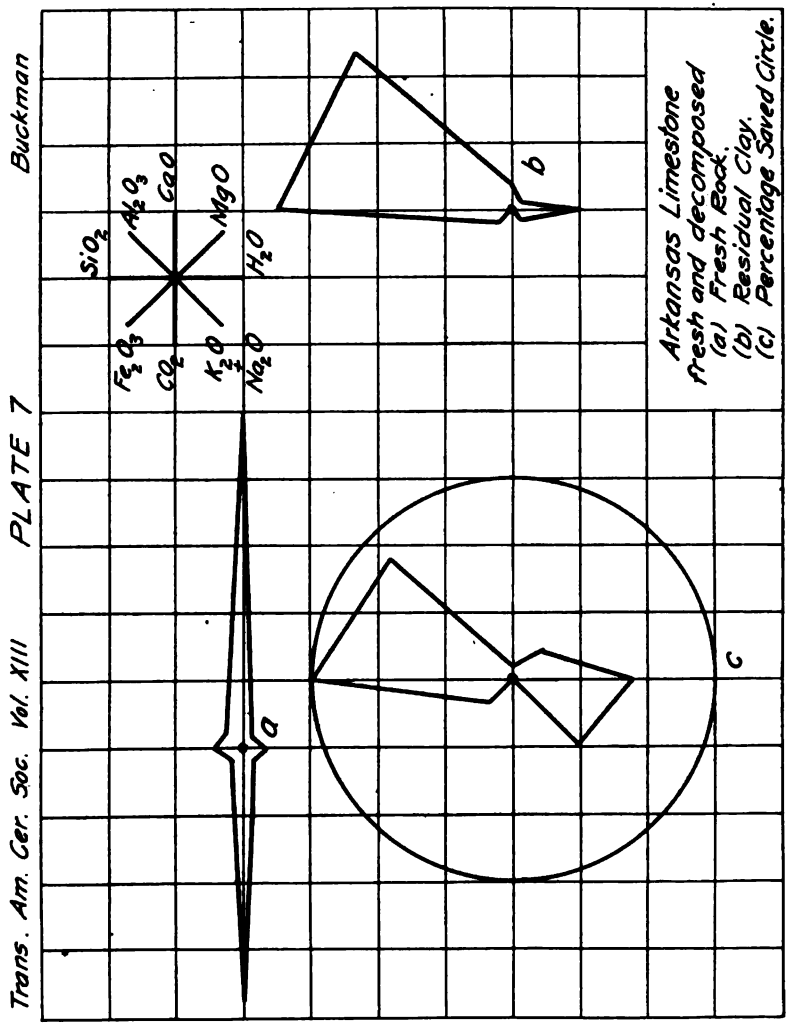

discussion of the investigational work on rock solubility and it is given below:[1]

[1] C. R. Van Hise, U. S. Geol. Survey, Mono XLVII, p. 515.

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Table Showing Per cent. of Constituents Lost during Formation of Residual Clays.

	K_2O	Na_2O	CaO	MgO	SiO_2	Fe_2O_3	Al_2O_3
Gneiss.....	83.52	95.03	100.0	74.70	52.45	14.35	000
Syenite.....	81.85	97.11	87.90	82.10	62.18	86.17	000
Diabase....	29.15	12.83	25.89	21.70	18.03	18.10	000
Diabase....	100.00	98.57	99.04	99.90	63.57	87.81	000
Basalt.....	61.69		84.53	74.10	32.99	50.17	000
Basalt.....	83.34	74.41	47.24	96.38	65.56	88.84	000
Diorite.....	38.75	84.87	97.30	97.17	37.31	21.03	000
Pyroxinite .	47.05	0.00	44.45	76.19	43.58	41.48	000
Argillite....	77.95	99.64	100.0	28.16	57.57	8.78	000
	67.70	70.31	76.26	72.27	48.14	46.30	000

This places the constituents in the order of Al_2O_3, Fe_2O_3, SiO_2, K_2O, Na_2O, MgO and CaO. Of course, if iron or silica should be used as a basis for calculation, as they often are, they would, in turn, be placed first. Ferrous oxide has not been considered as such from the fact that it generally changes to the ferric form. However, from its known solubility, it would probably come at the end of the list. The silica, which we are considering in this case, is not lost from the free quartz but from the silicates. However, such an average is not at all reliable as the differences between the percentages of several of the oxides are so small. A few analyses selected at random and added to these already cited would change completely the order of solubility. Nevertheless, such calculations, rough as they are, confirm in general, not only in the order of solubility of the chemical constituents, but the solubility of the minerals themselves.

We have studied thus far the decomposition of minerals, applied their data to the rocks themselves and have traced these rocks in their change from fresh aggregates to residual clays, making due allowance for physical forces. A summary, then, of the laws of rock resistance must embody the principles already evolved. It should be kept in mind,

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however, that these laws are not specific laws and can apply only when other factors are constant.

Laws of Rock Resistance.

1. The more basic a rock becomes the more rapid is decomposition, and the more acid, the less rapid.

2. An increase of sodium and potash accelerates chemical decomposition.

a. Increase of sodium over potash decreases relative resistance.

b. Increase of potash over sodium increases relative resistance.

3. The more magnesium and calcium present in a rock, the more rapid is chemical decomposition.

a. Increase of calcium over magnesium decreases resistance.

b. Increase of magnesium over calcium increases resistance.

4. Increase of iron in a rock lessens resistance.

5. Increase of aluminum checks decomposition.

6. Silica causes less rapid chemical decay.

Thus far, only the laws of rock-weathering have been dealt with and methods of rock decay indicated. It remains, then, to determine how this data may be applied in relation to the product, the residual clay. It is well known that a soluble material of any rock may exist in its residual clay either in an undecomposed mineral or in the clay solution itself. Soluble minerals go into solution so very gradually that a residual clay may contain many particles of minerals usually considered very soluble. Again, the power of adsorption of the solution surrounding clay particles is strong and materials may be held thus for a long time after their solution has occurred. Consequently, we may expect to find from the same kinds of rocks a graded series of clays according to the percentage of the soluble elements. This would account, then, for the many variations in chemical analyses of clays from the same districts. Two factors enter here to determine the

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composition of the residual clay. First, the extent to which physical forces have aided in the rock decay, and second, the degree with which chemical action has proceeded. When physical agents predominate, the composition of the residual clay may differ but little from the parent rock. It is the chemical forces that produce the great change. To a person interested in clay and its workings, the knowledge of what an analysis means and just why it occurs thus is of no uncertain value.

It is quite obvious that it is impossible to say, except in the most general terms, what the character and chemical composition of a residual clay from any particular rock may be. So many factors enter into this process which we call rock-weathering, that its complexity is multiplied many fold. That a limestone usually produces a ferruginous clay is well known. Granites may form sandy clays but the chemical composition of this residual clay must depend largely on the degree of chemical decay, other factors being, of course, equal. Rocks containing large per cents. of the ferro-magnesian minerals are likely to decompose into ferruginous clays, because weathering tends to concentrate the iron, as well as accentuate its presence by oxidation. In general, however, it may be said that rocks containing large percentages of a resistant element form a clay with as large or usually still larger per cent. of that particular constituent. Readily soluble materials may or may not be lost to a large degree according to their amounts in the parent rock, the form in which they are present and the conditions of weathering. This is illustrated by a clay from limestone being usually very poor in lime. Here the calcium carbonate is present in large amounts in the parent rock. Again, in many cases, the potash in granites may even show a gain in percentage in the resultant clay. Of course it is present in the fresh rock in small amounts which may partly account for its behavior.

We must not fail to call attention, in closing, to one fact, probably the most important in the study of the

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formation of residual clays. It is clearly apparent from every analysis shown in this discussion that no matter what the rocks or what may be their chemical compositions, their residues all bear a striking similarity to one another. This appears with particular clearness in all the charts shown of the fresh rocks and their residual clays. Weathering, in general, seems to tend toward the production, in all cases, of a common clay type when relationships are expressed in chemical terms, and all rocks are gradually resolved into this common type simply because their siliceous aluminates are the most resistant portion of their make-up.

In studying the general phases of clay formation, a fairly complete bibliography was acquired. In order to present clearly the sources of the ideas expressed in this paper and also in hopes that it may be of aid to others interested in this question of clay formation, it is herewith appended. A bibliography of the analyses of fresh rocks and their resultant residues has also been added.

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THE CONSTRUCTION OF A TWELVE-FOOT, POTTER'S UPDRAFT KILN.

By FRANK H. RIDDLE.

Assuming that a complete working drawing of a kiln would be of value to our "Transactions," I give herewith such a drawing of a kiln which I have used for some time.

It will be noted that in the following plates two distinct types of fire boxes are shown.

The box shown on all drawings, *i. e.*, the one fired through the cast iron fire door, is far superior to the box fired from the hob top. It is so constructed that one man alone can fire with ease. It also permits the coking of the coal before being pushed down to the hottest part of the box.

By use of the flue holes "F" it is possible to make an over-draft at will and force the heat under the floor and up the well hole. This permits of a much better distribution of heat and the resulting evenness of temperature in the top and bottom.

The flues are so distributed that they give air to each part of the fire, thus tending to produce better combustion.

Briefly the advantages and disadvantages of the new over-draft fire box over the old hob top fired fire boxes are as shown in the following table:

Advantages.

New over-draft box	Old hob top fired box
Easily operated by 1 man.	Low cost of construction.
Saves 20 per cent. in fuel.	
Much more uniform.	
Better control of heat.	
Longer life of box lining.	

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Disadvantages.

Requires close attention.	Poor combustion.
Higher cost of construction (not excessive).	Hard to get the heat in bottom.
	Requires two men to fire.
	Subject to reducing conditions in putting on new fires.

This new box has been in use three years and fired regularly. The only repairs in that time have been the replacing of a few grate bars and a new set of baffle plates. The iron door frames have shown no signs of warping.

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THE FUNCTION OF TIME ON THE VITRIFICATION OF A SHALE.

By A. V. Bleininger and T. L. Boys.

That time is an exceedingly important function in the maturing of clays and bodies is so well-known that the statement hardly needs repetition. Our attention is frequently called to the fact that a certain result may be obtained either by the application of a higher intensity of heat for a shorter time or a lower temperature for a longer time. The practical effect of the time factor we see constantly illustrated in the burning of pottery and other bodies, the softening of pyrometric cones, etc. It is a well-known fact in the case of the latter, that a difference of as much as a hundred degrees may be observed between the softening points determined in a small test furnace and a commercial kiln.[1] Yet there is a definite limit with reference to this matter depending upon the kind of body. To illustrate, it is obvious that a feldspar body may show the effect of long firing in a marked degree, while a calcareous composition is more indifferent in this respect. Even with reference to the former, certain limits must be clearly recognized. Thus it is not likely that a porcelain body ordinarily maturing at, say, cone 10, can be made to vitrify at cones 6 or 7 by increasing the time of firing within reasonable length.

In discussing the vitrification of clay, we are somewhat too prone to ascribe the closing up of the pore system entirely to the action of fluxes which cause incipient softening and the resulting lack of molecular cohesion due to the decreased viscosity. Under these conditions, contraction takes place, due to the forces which exert an inward pressure upon the surface of the substance. Yet this is by no means true. Part of the contraction is undoubtedly caused by the shrinkage of the colloidal portion of clays, since, indeed, such condensation is typical of amorphous substances in distinction from crystalline materials. We need think in this connection only of pure alumina, magnesia, zirconia, etc. The contraction of kaolin begins soon after the chemical water is drawn off, *i. e.*, when the substance is a typical amorphous body.

[1] Hoffmann, Sprechsaal, 44, 143–45.

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Lukas,[1] in an investigation of the fire shrinkage of such substances, determined the contraction suffered by small specimens of Zettlitz kaolin.

In Fig. 1 the results of measurements made upon these are given, showing clearly the different rates at which the condition of apparent equilibrium is approached as well as the rate at which the pore space is closed up at different temperatures. With regard to the first point, it is seen that at higher temperatures, constancy in porosity is approached more rapidly; and with reference to the second, it is clearly shown, that, as is to be expected, higher temperatures cause the shrinkage to be larger. This increase in shrinkage becomes small as the temperature rises. Thus while the gain in shrinkage between 1100° and 1200° is quite large, it is, of course, very much smaller between 1200° and 1300°. At still higher temperatures the values would tend to coincide more and more.

Mellor[2] has correlated the time effect as expressed by reburning a sagger body repeatedly at cone 8. He finds that the rate at which the contraction takes place may be represented by an expression resembling that for the speed of a bi-molecular reaction. This, of course, is but a coincidence. According to this "the change of contraction during each firing is proportional to the square of the contraction which is yet to be made."

The work to be described in this paper deals with a paving brick shale from Streator, Ill., the porosity-temperature curve of which is shown in Fig. 2. The shale is an excellent material, well-known for its high quality.

The shale, after disintegration, was made up with water into a fairly large lump, thoroughly kneaded and mixed, from which smaller cylinders were formed, weighing from 16–19 grams in the dry state. These were dried, and then slowly heated up in a small gas-fired muffle kiln to 650° C. until all of the carbon was burnt out. At this stage the average porosity was determined in the usual way by the absorption of water *in vacuo* and calculation from the formula: $100\ (W - D) \div (W - S) =$ per cent. poro-

[1] Zeitschrift für physikal. Chemie, 52, 327.
[2] Trans. English Ceramic Society, 9, 79.

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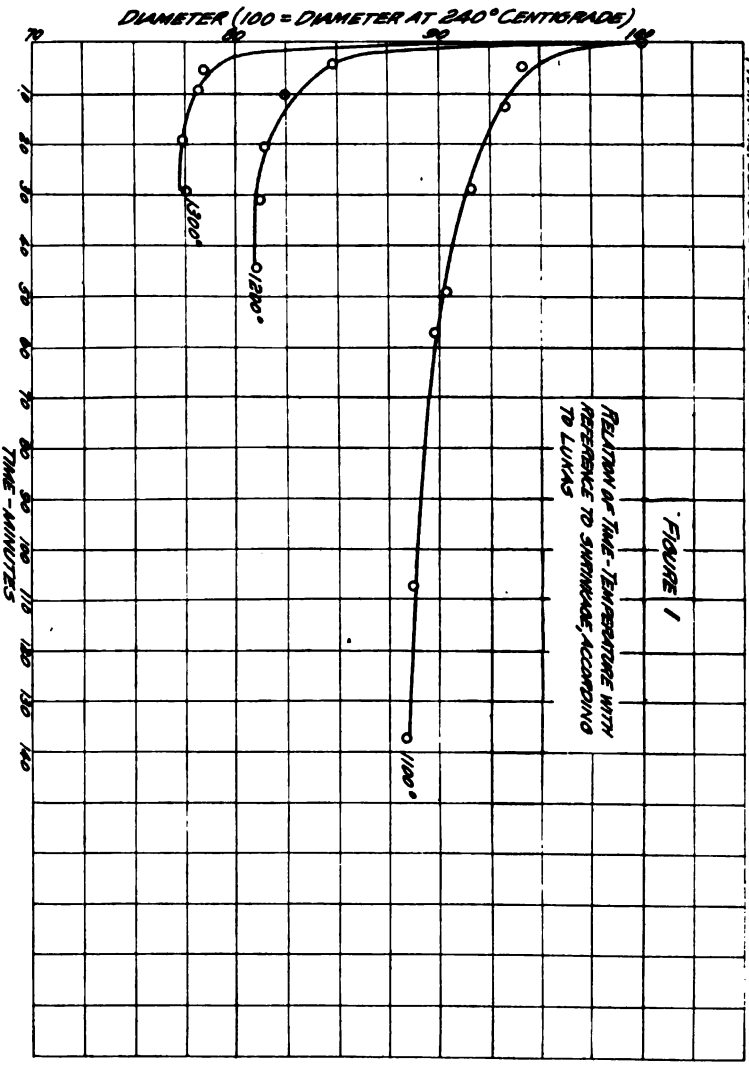

FIGURE 1

RELATION OF TIME-TEMPERATURE WITH REFERENCE TO SHRINKAGE, ACCORDING TO LUKAS

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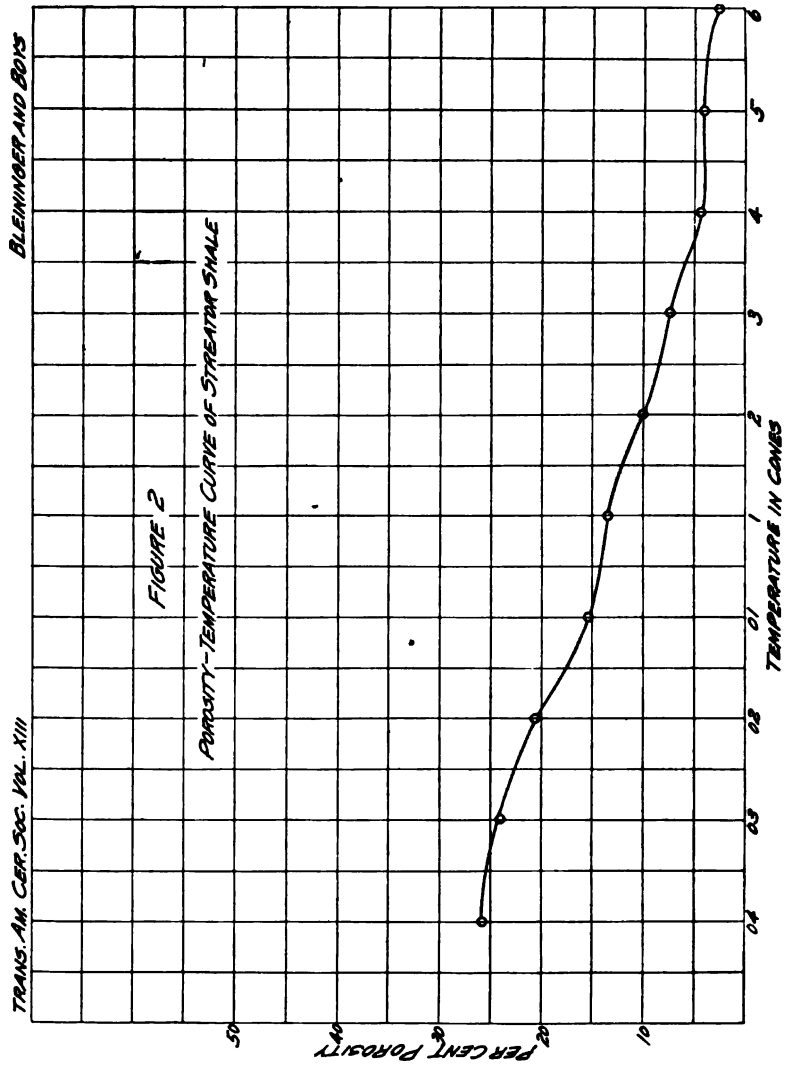

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sity, where D, W and S represent the dry, wet and suspended weights respectively. The average porosity was thus found to be 37.4 per cent.

The heating of these specimens to higher temperatures was accomplished in a small electric platinum resistance furnace, $1^1/_4''$ in diameter and 3" high, inside. After repeated trials, the zone of greatest temperature uniformity was determined. Within this zone the specimen was placed, supported by a small clay block. Notches were cut into the top of the latter so as to secure better heat distribution around the supported end of the cylinder. The electric current was regulated by means of two rheostats. The specimens were heated up according to predetermined schedules which are shown in Fig. 3. In each case the heating curve was a straight line, ending at 900° C., 950°, 1000°, 1050°, 1100°, 1150°, and 1200°. For each of these points the porosity of a specimen was determined, thus requiring $7 \times 6 = 42$ furnace runs. The rates of the six heating schedules varied from 16 to 2.05° C. per minute.

The results of the work are represented in Fig. 4, where the curves for the temperatures lower than 1100° have been omitted, owing to the fact that they became practically parallel to the abscissa at fairly high porosities. The 1100° and 1150° curves show a distinct slope with the highest time, and, theoretically, would meet the minimum porosity of the 1200° curve after 1360 minutes. Similarly, the 1150° curve would meet the minimum porosity line after 970 minutes. This would be equivalent to saying that a heating treatment, such that 1100° is reached at a constant rate in 1360 minutes, would bring about the same result as the heating up at the constant rate of 2.05° per minute to 1200°, corresponding to 585 minutes. Whether this statement is borne out by the fact cannot be said at present. To prove this experimentally, the time should have been lengthened so that the curves would intersect. Under the conditions prevailing at the time this experiment was carried on, this could not be done.

An examination of these curves will show, as is to be expected, that the drop in porosity or, generally speaking, the rate of vitrification is very much greater at the beginning of the heat-

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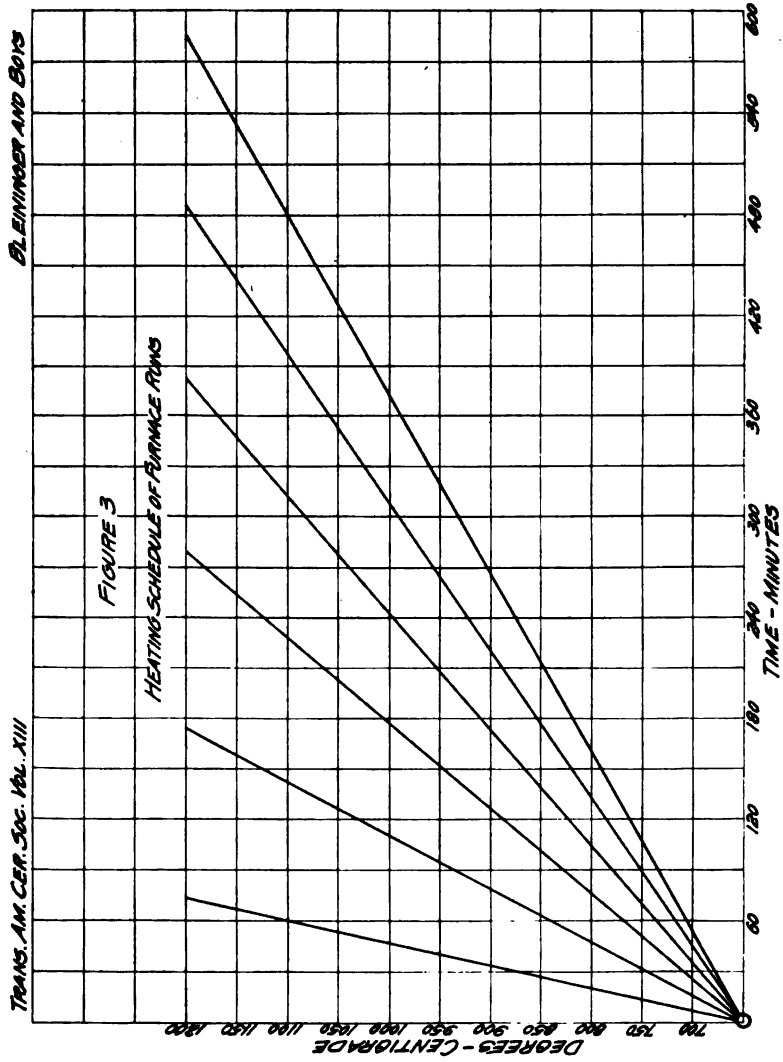

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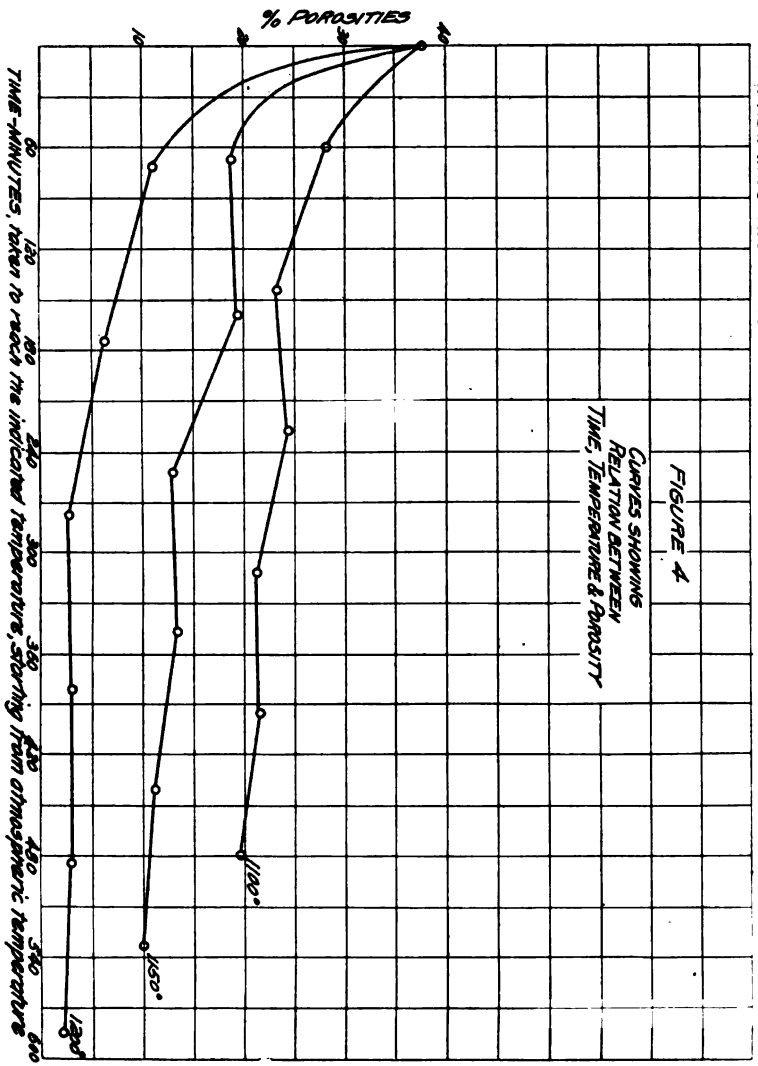

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FIGURE 4.

CURVES SHOWING RELATION BETWEEN TIME, TEMPERATURE & POROSITY

BLEININGER AND BOYS

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ing and gradually tapers off as it is continued. Thus, during the first 72 minutes the rate of vitrification is about 7.5 times as great as that between 72 and 174 minutes, reduced to porosity drop per minute. This rate of vitrification does not follow the rule suggested by Mellor.

Considering points of equal porosity, it is observed, for instance, that a porosity of 20 per cent. is obtained at 1100° after 480 minutes, while the same point is reached in a 68-minute run up to 1150° and in considerably less time in the 1200° run. Similarly, the 10 per cent. porosity is reached in a 72 minute heating up to 1200° and after 536 minutes up to 1150°.

It is proposed to carry on further work along these lines with longer time and closer temperature intervals so that numerous definite intersection points may be obtained. It is also proposed to bring in the question of heat absorption of clays.

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EFFECT OF COMPOSITION ON THE STRENGTH OF PORCELAINS.[1]

By LESTER OGDEN, Columbus, Ohio.

Object.—The object of this research was, as the title implies, to learn if possible the effects of a varying composition on the toughness of porcelains.

Previous Work.—The writer knows of but one other piece of work along this line—that of Mr. Ellsworth Ogden[2]. While the plan of attack and method of procedure in this work were considerably different from those employed in the above-mentioned research, the results are, nevertheless, comparable.

Plan of Attack.—To limit the field of study to one that could be thoroughly worked over in the time allowed, it was decided to limit the number of variants. The field chosen was designed to cover and overlap the field of commercially workable porcelains of three components, maturing at cone 10. To this end the clay content was varied between 20 per cent. and 60 per cent. (inclusive), the feldspar between 10 per cent. and 50 per cent., and the flint making up the balance. The field covered is most clearly seen on the triaxial diagram (Fig. 1).

Table of Percentage Composition.

Feldspar : flint :: 1 : 3	A–1	A–2	A–3	A–4	A–5	A–6	A–7	A–8	A–9
Clay	60	55.0	50.0	45.0	40	35.0	30.0	25.0	20
Flint	30	33.75	37.5	41.25	45	48.75	52.5	56.25	60
Feldspar	10	11.25	12.5	13.75	15	16.25	17.5	18.75	20
Feldspar : flint :: 3 : 5	**B–1**	**B–2**	**B–3**	**B–4**	**B–5**	**B–6**	**B–7**	**B–8**	**B–9**
Clay	60	55	50	45	40	35	30	25	20
Flint	25	28⅛	31¼	34⅜	37½	40⅝	43¾	46⅞	50
Feldspar	15	16⅞	18¾	20⅝	22½	24⅜	26¼	28⅛	30

[1] Thesis at the Ohio State University under the direction of Ross C. Purdy.
[2] Trans. A. C. S., Vol. VII, p. 370.

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Table of Percentage Composition (*Continued*).

Feldspar: flint :: 1 : 1	C–1	C–2	C–3	C–4	C–5	C–6	C–7	C–8	C–9
Clay.....	60	55	50	45	40	35	30	25	20
Flint.....	20	22½	25	27½	30	32½	35	37½	40
Feldspar .	20	22½	25	27½	30	32½	35	37½	40
Feldspar: flint :: 5 : 3	**D–1**	**D–2**	**D–3**	**D–4**	**D–5**	**D–6**	**D–7**	**D–8**	**D–9**
Clay	60	55	50	45	40	35	30	25	20
Flint.....	15	16⅞	18¾	20⅝	22½	24⅜	26¼	28⅛	30
Feldspar .	25	28⅛	31¼	34⅜	37½	40⅝	43¾	46⅞	50
	V–1	**V–2**	**V–3**	**V–4**	**V–5**	**V–6**	**V–7**	**V–8**	**V–9**
Clay.....	60	55	50	45	40	35	30	25	20
Flint.....	30	35	40	45	50	55	60	65	70
Feldspar .	10	10	10	10	10	10	10	10	10
	W–1	**W–2**	**W–3**	**W–4**	**W–5**	**W–6**	**W–7**	**W–8**	**W–9**
Clay.....	60	55	50	45	40	35	30	25	20
Flint.....	25	30	35	40	45	50	55	60	65
Feldspar .	15	15	15	15	15	15	15	15	15
	X–1	**X–2**	**X–3**	**X–4**	**X–5**	**X–6**	**X–7**	**X–8**	**X–9**
Clay.....	60	55	50	45	40	35	30	25	20
Flint.....	20	25	30	35	40	45	50	55	60
Feldspar .	20	20	20	20	20	20	20	20	20
	Y–1	**Y–2**	**Y–3**	**Y–4**	**Y–5**	**Y–6**	**Y–7**	**Y–8**	**Y–9**
Clay.....	60	55	50	45	40	35	30	25	20
Flint.....	15	20	25	30	35	40	40	50	55
Feldspar .	25	25	25	25	25	25	25	25	25
	Z–1	**Z–2**	**Z–3**	**Z–4**	**Z–5**	**Z–6**	**Z–7**	**Z–8**	**Z–9**
Clay.....	60	55	50	45	40	35	30	25	20
Flint.....	10	15	20	25	30	35	40	45	50
Feldspar .	30	30	30	30	30	30	30	30	30

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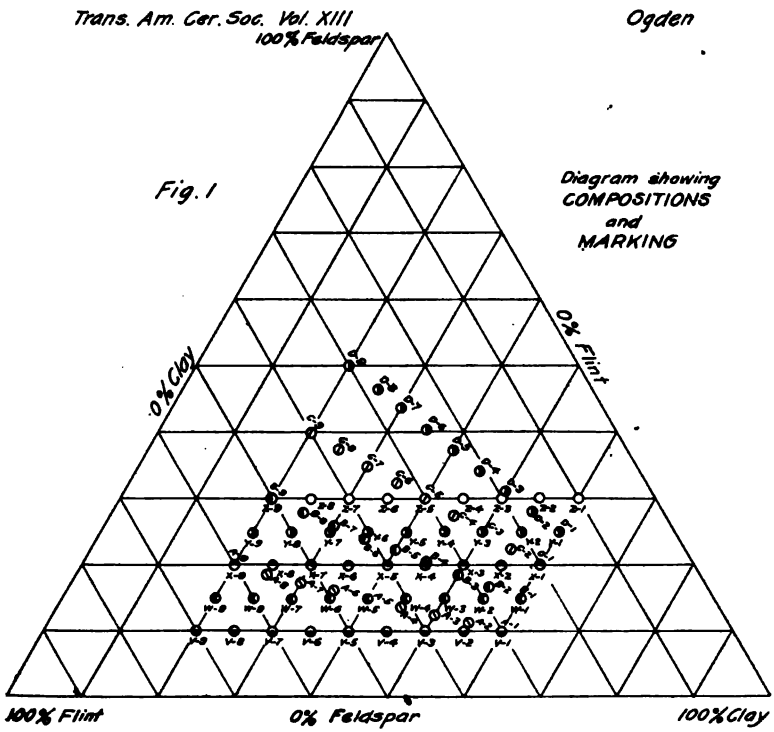
Materials Used.—To further approach commercial practice, the clay content was made up of several clays in the following proportions:

	Per cent.
Georgia Washed Kaolin	25
English China Clay, No. 7	25
Harris Dillsboro Kaolin	25
English Ball Clay, No. 12	12½
Tennessee Ball Clay, No. 9	12½

Golding's flint and Brandywine feldspar were used.

Marking.—All bodies having the same number have



the same clay content. All bodies having the same letter have either the same content of feldspar or a constant

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ratio between feldspar and flint. Series A, B, C and D represent the latter, while V, W, X, Y and Z, the former. To obtain a series with a constant content of flint, it is only necessary to take the last five letters in order and have the numerals form a regular sequence, thus, V-1, W-2, X-3, Y-4, Z-5, or V-4, W-5, X-6, etc.

Manufacture.—Five kilograms (11 lbs.) of each body were carefully weighed up and ground with six quarts of water for exactly thirty minutes in a Bonnot ball mill of three gallon capacity. The slip was then screened through a hundred-mesh sieve and filter-pressed. The filter-pressed bodies were then wedged on a plaster block, placed in covered jars and allowed to age in a warm room for six weeks.

The trial pieces were made by hand-pressing in plaster moulds. To measure shrinkage and translucency, as well as toughness and absorption, necessitated the making of three different shaped pieces.

For abrasion and absorption, a disc 3/4″ thick by 2–3/4″ in diameter was selected, and ten for each body made. For shrinkage, a bar 4″ x 3/4″ x 3/8″ was made, while for translucency, a wedge 7/8″ x 3/8″ at the base and tapering to a thin edge.

Drying and Burning.—The trial pieces were carefully dried in a moderately warm room, free from draught. They showed no cracking and very little warping. After being thoroughly dried, they were biscuited to cone 010 in the largest of the down-draft kilns of the Ceramic Department at the Ohio State University.[1]

The cone 010 biscuiting was to give them the durability to permit their being transported to Zanesville, where, through the courtesy of Mr. Morton, they were burned in a regular burn at the Mosaic Tile Works. The fourteen saggars containing the trials were set together and, as there

[1] This kiln has given excellent results, and it would have been possible to have given them a uniform burn to cone 10 in it, but as the aim thus far had been to approach factory conditions it was decided to have the trials burned to cone 10 in a large commercial kiln.

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was not a half cone difference between the top and bottom of the kiln, received a very uniform burn.

Description of Burned Trials.—Up to and through the biscuit burn no cracking had taken place, but during the last burn many of the pieces cracked; in many instances all of the ten trial pieces for a given body were cracked. It was noted that badly cracked bodies are, with but very few exceptions, those containing 40 or more per cent. flint.

The degree of vitrification and comparative translucency of the several trials is shown by the data.

Abrasion.—The abrasion test used was the familar rattler test. This test was conducted in four periods of fifteen minutes each. The rattling was done in the Sheibell mill, same as used by Ellsworth Ogden. The speed of the mill was sixty revolutions per minute. The charge consisted of 150 pounds of iron stars: 125 pounds of stars weighing eighteen to the pound, and 25 pounds of larger ones weighing six to the pound. A test on two sets of commercial porcelain floor tile, $1-1/2'' \times 3''$, ten to the set, gave the following results:

	1st charge	2nd charge
Loss in per cent., end of 15 min.....	5.83	5.93
" " " 30 "	7.49	7.69
" " " 45 "	8.50	9.20
" " " 60 "	9.26	10.08

As mentioned above, many of the bodies had cracked so badly that there were not sufficient trial pieces for a rattler test so it was decided to rattle only those bodies where at least six trial pieces showed no signs of cracking. This cut the number of bodies to be rattled from 72 to 36. Five trial pieces each, of three bodies, were put into the mill at the same time, making twelve charges to be rattled for four periods of fifteen minutes each. In order to have the results as nearly comparable as possible, and to get away from a part, at least, of the adverse criticism for using

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a pointed abrasion, sufficient stars were secured, through the kindness of Mr. Monroe Kittle, Ohio Malleable Iron Works, to permit an entirely new charge of stars every three hours. This meant that one charge of stars must take care of three charges of trials. Instead of rattling first one set of trials clear through, each of the three sets were given a fifteen-minute period—the stars standardized—and then all given another fifteen minutes in the reverse order, thus calling the charges A, B and C.

1st A,	2nd B,	3rd C,	rattled 15 min. star standardized.
6th A,	5th B,	4th C,	" 15 " " "
7th A,	8th B,	9th C,	" 15 " " "
12th A,	11th B,	10th C,	" 15 " " "
			Stars all cast out.

While this does not give each charge exactly the same treatment for a given period, the culminative effect of the four periods should be very nearly the same.

Absorption.—The absorption data was obtained by weighing the test pieces before and after a 48-hour soaking period.

Translucency.—The measure of translucency here given is the thickness of the body in millimeters required to shut out the light of a 16-candle power incandescent lamp, and was obtained as follows: A box of sufficient size to accommodate the above-mentioned light, and having one side of zinc in which there was a narrow slit about half an inch long, was taken into a dark room, where, with the only light available coming through the slit in the zinc, it was very easy to slide one of the wedges up or down past this slit until the light was just shut out. This point, marked on the wedge, was calipered.

The result of these tests, together with shrinkage and absorption, follows.

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	Rattler loss in per cent.				Shrinkage in		Per cent. absorption	Translucency in millimeters
	15 min.	30 min	45 min.	60 min.	Drying	Fire		
A-1.....					3.36	8.53	9.70	3.2
A-2.....					3.63	7.77	6.34	3.4
A-3.....					3.09	7.21	4.55	3.6
A-4.....					2.82	8.48	4.23	3.9
A-5.....					2.82	8.48	3.67	3.6
A-6.....					2.82	8.99	1.77	4.4
A-7.....					1.78	9.41	1.56	5.6
A-8.....					1.26	8.35	0.91	5.3
A-9.....					1.52	7.61	0.66	6.2
B-1.....	4.77	6.50	8.02	9.32	3.36	9.04	4.81	3.6
B-2.....	4.68	6.17	7.23	8.29	3.09	9.28	3.95	3.9
B-3.....	2.27	3.10	4.14	4.55	2.56	9.74	1.91	4.6
B-4.....					2.82	8.99	0.15	4.6
B-5.....					2.56	8.72	0.25	5.2
B-6.....					2.56	9.23	0.19	5.5
B-7.....					2.82	7.93	0.29	5.6
B-8.....					2.56	8.72	0.33	6.7
B-9.....					1.26	7.34	0.23	7.0

	Rattler loss in per cent				Shrinkage in		Per cent. absorption	Translucency in millimeters
	15 min.	30 min.	45 min.	60 min.	Drying	Fire		
C-1.....	4.03	5.09	6.36	7.43	3.63	9.84	3.60	3.2
C-2.....	3.63	5.12	6.43	7.28	3.63	9.84	2.89	3.6
C-3.....	2.51	3.56	4.61	5.45	2.30	9.97	0.26	4.5
C-4.....	2.68	3.71	4.33	4.54	2.82	10.04	0.15	4.4
C-5.....	2.19	2.98	4.18	4.78	2.56	9.21	0.09	5.3
C-6.....	2.35	3.34	4.32	4.91	2.30	8.95	0.00	5.8
C-7.....	2.31	3.08	3.85	4.23	2.04	7.14	0.00	6.6
C-8.....	2.06	2.80	3.74	4.30	2.04	6.63	0.04	7.4
C-9.....	1.83	2.75	3.67	4.58	1.52	5.88	0.13	7.6
D-1.....	5.66	7.18	8.93	10.23	3.89	10.65	1.39	3.8
D-2.....	4.22	6.34	7.39	8.24	3.36	10.08	1.72	3.5
D-3.....	4.52	5.76	6.79	7.40	2.56	9.74	0.05	4.7
D-4.....	3.10	4.34	6.21	7.86	2.56	9.74	0.05	5.2
D-5.....	2.42	3.43	4.44	5.05	3.36	8.53	0.00	5.7
D-6.....	2.93	4.29	5.46	6.03	2.30	8.95	0.05	5.8
D-7.....	2.14	3.31	4.09	4.67	2.30	7.92	0.00	6.8
D-8.....	2.42	3.54	4.47	5.41	2.04	5.07	0.04	8.0
D-9.....	2.17	3.44	4.71	5.62	1.78	5.85	0.00	8.0

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	Rattler loss in per cent				Shrinkage in		Per cent absorption	Translucency in millimeters
	15 min.	30 min.	45 min.	60 min.	Drying	Fire		
V-1	5.36	8.58	11.37	13.94	3.36	8.53	9.70	3.2
V-2	6.10	9.68	12.63	15.36	3.09	7.73	8.45	3.2
V-3	5.18	8.71	11.82	14.73	3.09	6.18	9.60	3.1
V-4					2.82	5.91	9.08	3.2
V-5					2.56	5.12	8.00	3.3
V-6					2.82	4.36	8.43	3.7
V-7					2.04	4.59	7.45	3.8
V-8					1.52	4.06	7.47	4.2
V-9					2.30	3.83	7.00	4.7
W-1	4.77	6.50	8.02	9.32	3.36	9.04	4.81	3.6
W-2	1.06	2.55	4.26	5.54	3.36	9.04	4.69	3.3
W-3					2.82	8.99	3.81	3.5
W-4					3.36	9.04	3.08	4.0
W-5					2.82	8.48	3.67	3.6
W-6					3.63	8.29	2.84	4.1
W-7					2.04	8.16	2.64	3.6
W-8					2.30	7.92	2.32	4.5
W-9					1.78	6.97	2.03	4.9

	Rattler loss in per cent				Shrinkage in		Per cent. absorption	Translucency in millimeters
	15 min.	30 min.	45 min.	60 min.	Drying	Fire		
X-1	4.03	5.09	6.36	7.43	3.63	9.84	3.60	3.2
X-2	4.42	6.10	7.15	8.21	3.09	10.30	2.85	3.6
X-3	2.33	3.60	4.45	5.09	3.36	11.11	2.28	4.1
X-4	2.30	3.34	3.97	4.39	3.09	10.31	1.08	4.7
X-5	1.96	2.94	3.73	4.12	2.30	9.46	0.58	4.8
X-6					1.78	9.41	0.74	5.6
X-7					2.56	8.20	0.75	5.4
X-8					1.52	7.61	0.85	5.7
X-9					1.52	7.61	0.66	6.2
Y-1	5.66	7.18	8.93	10.23	3.89	10.65	1.39	3.8
Y-2	5.19	6.49	7.57	8.22	2.82	10.54	1.97	4.2
Y-3	2.51	3.56	4.61	5.45	2.30	9.97	0.26	4.5
Y-4	2.82	3.83	4.84	5.65	3.63	9.84	0.15	5.0
Y-5					2.56	8.71	0.36	5.5
Y-6					2.56	9.23	0.14	5.6
Y-7					2.56	8.71	0.39	5.7
Y-8					1.52	6.09	0.41	6.3
Y-9					1.26	6.83	0.42	6.9

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	Rattler loss in per cent.				Shrinkage in		Per cent. absorption	Translucency in millimeters
	15 min.	30 min	45 min.	60 min.	Drying	Fire		
Z-1.....	5.02	6.55	7.64	8.51	3.63	10.36	1.64	4.4
Z-2.....	4.33	5.86	7.15	8.02	3.09	10.31	0.53	4.5
Z-3.....	3.38	4.8	5.49	6.34	2.82	10.54	0.05	4.6
Z-4.....	2.71	3.54	4.38	4.80	2.82	10.54	0.05	5.5
Z-5.....	2.19	2.98	4.18	4.78	2.56	9.21	0.09	5.3
Z-6.....	1.98	2.78	3.57	4.17	2.56	8.72	0.05	5.9
Z-7.....					2.56	8.71	0.09	5.8
Z-8.....					2.30	8.44	0.18	6.5
Z-9.....					1.26	7.34	0.23	7.0

CONCLUSIONS.

The data at hand seems to warrant the following statements:

First.—That in a three-component porcelain maturing at cone 10:

(*a*) The feldspar content should not be less than 15 per cent.

(*b*) The clay should not exceed 50 per cent.

(*c*) The flint should not be under 30 per cent.

Second.—That within these limits, with a given content of clay, the toughness increases with an increase in flint, and a simultaneous decrease in feldspar.

Third.—That with feldspar constant the toughness increases with increase in flint and simultaneous decrease in clay.

Fourth.—That with constant flint there is little or no evidence of toughness, varying directly as either of the other ingredients.

Fifth.—That the toughness of a porcelain is dependent more upon the amount of flint present than upon either of the other two ingredients, and that within the limits of this research, the percentage of flint to be used for a strong porcelain should be very close to 35. With 35 per cent. flint there seems to be very wide range of variation in clay and feldspar which produce tough bodies.

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The object sought in making the 15-minute periods was not attained, due to the difference in degree of vitrification of the various bodies. The idea of making the 15-minute rattler periods was to determine the relative liability of the various bodies to chipping. This could be shown by the percentage of the total loss that the bodies had suffered during the first 15-minute period, and would necessitate equal degree of vitrification of the bodies.

DISCUSSION.

Mr. Humphrey: Slow cooling has the same effect in vitrified china as annealing does in glass. If cooled slowly, we obtain a tough body; and if cooled too rapidly, a brittle body. While the composition is important, slow cooling is equally as important a factor.

Mr. Riddle: I should like to ask Mr. Humphrey which he thinks is the most important stage of cooling in which to go slowly; that is, whether at a high temperature or at a low temperature. I have had occasion to try slow cooling on paving brick, and have found some difference.

Mr. Humphrey: My process was cooling as slowly as possible through the whole time.

Mr. Bleininger: It seems to me that cooling should be carried on more slowly during the first stage. We know, naturally, that the drop in temperature is greatest beginning at the highest temperature, or the finishing temperature of the kiln. Consequently, it appears to me that the cooling might be retarded particularly during the first stage. Of course, this is a general consideration only; we really have no data available to throw light on this subject and I realize that in several instances that have come to my knowledge exactly the reverse seems to be true.

Mr. Coulter: In the experience that I had in cooling brick fast and slowly,[1] I found that when the bricks were very hot, I could not injure them by cooling them fast.

[1] Trans. A. C. S., Vol. IX, p. 618.

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It was only when they reached a temperature of about seven hundred degrees that injury could be done to them by fast cooling. The amount of injury was indicated by the cracking heard in the kiln. At very high temperatures, above seven hundred degrees, the cold air could be forced in with a fan, without producing injury. The degrees mentioned are Centigrade not Fahrenheit.

Mr. Purdy: I know of an instance in which the waste heat of a cooling floor-tile kiln is being withdrawn until the kiln loses color, at which time they stop drawing off heat and finish the cooling under natural draft, and this without effect on the toughness of the tile.

Mr. Humphrey: In making window-glass, the pieces are made and cooled quickly; and before being annealed, the glass is heated again until it becomes almost viscous. Its shape can then be readily changed, the glass flattening out almost like rubber. From that point, the glass gradually cooled and, of course, annealed. Whether it is necessary to go to that temperature in order to obtain proper annealing, I do not know.

Mr. Purdy: In annealing lamp-chimneys, they use hot oil, hence, not a very high temperature.

Mr. Stover: Is it not possible that we might look in this direction for relief from dunting?

Mr. E. D. Gates: In cooling a kiln one may avoid cooling cracks by dropping rapidly until dull red is reached, and then cooling slowly. This is all a matter of guesswork, however. When the ware is at a high temperature, the air will be heated before reaching the ware; but when the temperature decreases, any cold air going through the kiln-walls will strike the pieces when it is still cold. I have not been able to place the temperature point, except to draw the line at about a red heat. It would be interesting to bring out the point whether there is a difference between cooling for annealing and for other purposes.

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SOME COEFFICIENT OF EXPANSION DATA ON PORCELAIN MADE FROM EUROPEAN MATERIALS.

By A. S. WATTS.

For these determinations the following materials were used:

NORWEGIAN FELDSPAR.

SiO_2	65.71
Al_2O_3	18.48
CaO	0.38
MgO	0.21
K_2O	11.97
Na_2O	3.03
Loss	0.36
	100.14

Fineness of Grain.—Finer than 5000 mesh per cm^2. —92.8 per cent.. Remains in suspension in neutral distilled H_2O—10 cm. deep.

20.01%	settled in 1 minute.					
33.01%	remained suspended	1	minute, settled in	5	minutes.	
9.29%	"	"	5	"	"	20
36.70%	"	"	more than 20 minutes.			
99.01						

HOHENBOCKA SAND.

SiO_2 99.68%

Fineness of Grain.—Finer than 5000 mesh per cm^2. —100 per cent. Remains suspended in neutral distilled H_2O—10 cm. deep.

6.3%	settled in 1 minute.						
10.6%	remained suspended	1	minute, settled in	5	minutes.		
14.7%	"	"	5	"	"	10	"
15.9%	"	"	10	"	"	20	"
55.0%	"	"	more than 20 minutes.				
102.5							

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CALCINED ZETTLITZ KAOLIN.

Not analyzed

Fineness of Grain.—All passed 5000 mesh per cm^2. Remained suspended in neutral distilled H_2O—10 cm. deep.

2.7%	settled in 1 minute.						
8.3%	remained suspended		1 minute,	settled in		5 minutes.	
12.0%	"	"	5	"	"	5	"
7.7%	"	"	10	"	"	20	"
69.0%	"	"	20	"			
99.7							

ZETTLITZ KAOLIN.

SiO_2	47.21
Al_2O_3	37.23
Fe_2O_3	0.76
KNaO	0.61
CaO	0.26
MgO	trace
Combined H_2O	14.16

Rational Analysis.

Clay substance	94.07
Quartz	2.20
Feldspar	3.8

The standard kaolin of Europe.

HALLISCHER THONE.

SiO_2	70.36
Al_2O_3	20.64
Fe_2O_3	0.53
KNaO	0.21
CaO	0.08
MgO	0.09
Combined H_2O	8.13

Rational Analysis.

Clay substance	56.50
Quartz	40.30
Feldspar	3.20

Clay substance content about as plastic as kaolin.

LOTHAINER THONE.

SiO_2	59.37
Al_2O_3	29.37
Fe_2O_3	0.71
KNaO	0.30
CaO	0.08
Combined H_2O	10.26

Rational Analysis.

Clay substance	75.40
Quartz	22.35
Feldspar	2.25

A very plastic ball clay.

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ENGLISH CHINA CLAY.

SiO_2	47.9
Al_2O_3	38.16
Fe_2O_3	0.49
CaO	trace
KNaO	1.28
Combined H_2O	12.31

Rational Analysis.

Clay substance	95.4
Quartz	1.0
Feldspar	3.6

The porcelains were made by ball mixing for 2 hours and test pieces by pressing in plaster moulds.

The firing was in two stages of about 24 hours each, the first reaching cone 010 and the second cone 15.

After the firing process, the pieces of porcelain were carefully ground on a carborundum wheel to the desired size and the two ends sharply pointed.

APPARATUS FOR DETERMINATION OF COEFFICIENT OF EXPANSION.

The apparatus used for these determinations, and shown in the accompanying illustration, consists of a

glass cylinder enclosed at both ends with metal caps and in the center of each cap, a bearing of quartz. The lower bearing is stationary and the upper free to move

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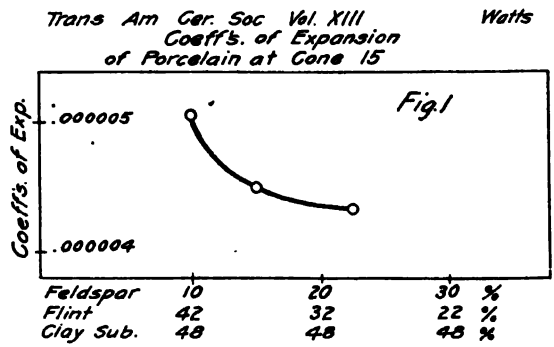
back and forth. Any change of position of this upper bearing is communicated through a lever on knife-edge pivots to a long lever which also acts as a pointer on a dial.

This trial piece, which is in the form of a pencil pointed at both ends, is first placed in water until it reaches a constant temperature. It is then carefully measured and placed between the bearings of the glass cylinder which has been brought to the same temperature as the trial piece. The pointer on the dial is then adjusted to read zero, after which steam is introduced into the cylinder until the trial piece has reached a constant temperature of 100° C. when a record is made of the expansion of the trial piece as indicated by the pointer upon the dial. The record thus obtained is reduced to value for 1 cm. length through one degree Centigrade change in temperature which is the coefficient of expansion of the material being tested.

THE EXPERIMENTS.

To determine the influence of the variation of flint and feldspar, I made a series with Zettlitz kaolin, constant at 48 per cent. The test pieces with more than 22 1/2 per cent. feldspar were too badly warped to be used and those with less than 10 per cent. feldspar were not matured so the series was necessarily limited. The resultant curve is as shown:



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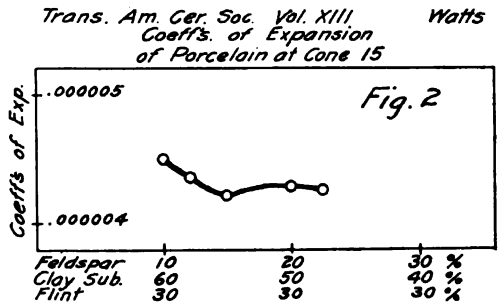
Within these limits a substitution of feldspar for flint reduces the coefficient of expansion.

To determine the influence of the variation of feldspar and clay, I made a second series with flint constant at 30 per cent. The clay substance was introduced from Zettlitz kaolin and I give you, in Fig. 2, the results of this series:



From the above, it would seem that within these limits, the replacing of feldspar by clay substance or *vice versa* doers not materially change the coefficient of expansion. The limits within which a series of either the clay-feldspar variation or the flint-feldspar variation can be made at cone 15, is too small to draw any but general conclusions.

The variation of the flint-clay content can be successfully worked over a longer range and I now made a series with 15 per cent. feldspar constant, and varied the flint and clay substance.

From the following curve it is apparent that the substitution of flint for clay substance has fully as much influence upon the coefficient of expansion as results from the substitution of flint for feldspar.

Since flint seems the active agent in causing variation of coefficient of expansion, it seemed important to determine if a substitute for it could be found which would possess this same property. I decided to try clay calcined at a high temperature. The clay substance

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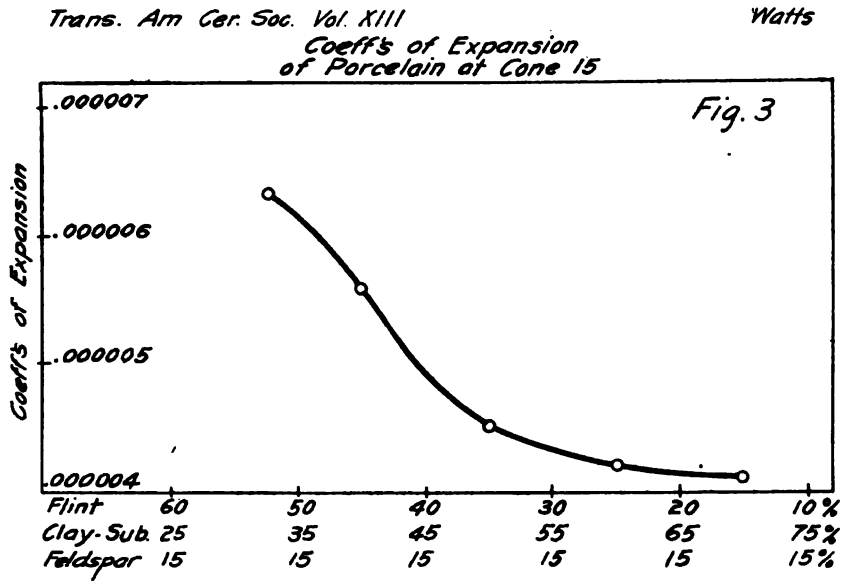
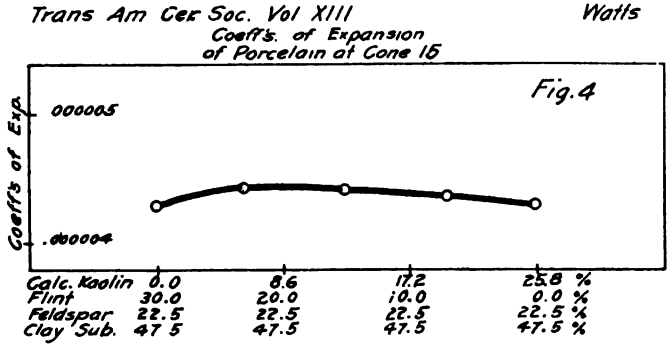


I utilized was Zettlitz kaolin calcined at cone 16 and ground. The results of varying the flint by substitution of this calcined kaolin is as shown in Fig. 4.



The results of this series indicate that calcined kaolin has practically the same effect as flint on the coefficient of expansion.

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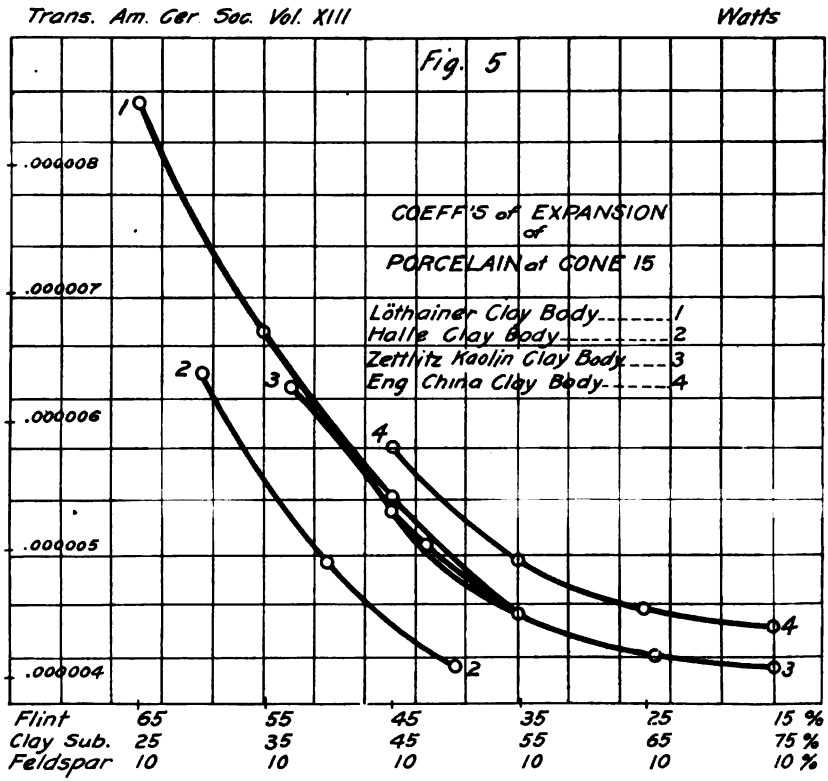
The question now arises whether the type of clay substance introduced effects the coefficient of expansion. To test this I made up parallel series using Lothainer clay, Halle clay, Zettlitzer kaolin and English china clay, all with 10 per cent. feldspar and with flint and clay substance variable. The test results on these series I show you in Fig. 5.



In this study we must bear in mind that the flint in Lothainer and Hallescher clays was partly introduced as natural impurity and undoubtedly not as fine-grained as the mill-ground flint. According to Seger, this would cause the body to have a lower coefficient of expansion so that curves 1 and 2 are both doubtless low and this is

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more pronounced in No. 2 than in No. 1, since No. 2 contained a higher per cent. of natural silica sand than did No. 1.

The extent of the influence of fine grinding of flint upon the coefficient of expansion, I did not determine, but the Hallescher ton and Zettlitz kaolin are very similar in all their physical properties, as well as chemical compositions aside from the excess of flint in the former and if this great difference in coefficients is due to the size of grain of the flint introduced, it appears as important a factor as the amount of flint added.

A comparison of these results with the findings of Dr. Seger, who worked with similar materials, is especially interesting.

To counteract crazing in glazes, Seger recommends increasing the coefficient of expansion of the body and gives the following methods for accomplishing this result.[1]

Method A.—*Decreasing the content of the body in plastic bonding material, with simultaneous increase of the content of silica.*

This is checked by my finding as shown in Fig. 3.

Method B.—*Replacement of a part of the clay-substance arising from kaolin by that coming from plastic clay.*

My work along this line is very unsatisfactory since the plastic clay employed contained sand which was coarser than the pulverized flint used with the other clays. According to Seger, this would decrease the coefficient of expansion and tend to neutralize the influence of the plastic clay toward an increase in the coefficient. However, the data shown in Fig. 5 confirms the findings of Seger with the exception of curve 4, which is of a body containing English china clay.

A peculiarity of this clay is that, although similar in chemical composition to kaolin, it imparted to the body, in which it replaced kaolin, a much higher coefficient of expansion. I do not offer any explanation for this phe-

[1] "Seger's Collected Writings," Vol. II, p. 577.

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nomena but call attention to the fact that wherever used in place of kaolin, English china clay lowers the maturing temperature of the body and the trials here tested showed evidence of over-maturity as indicated by bloating.

Method C.—*Decrease in the content of feldspar.*

The changes in composition of my trials were by substitution and not by straight addition, hence, I have no results directly comparable with Seger. My data, shown in Fig. 1, indicate that replacement of feldspar by clay substance causes little change in coefficient of expansion. The data shown in Fig. 2, however, indicate that replacement of feldspar by flint increases the coefficient of expansion to a marked degree. Since a straight reduction of feldspar means a proportionate increase in flint—clay substance content, the result would be a combination of that shown in Fig. 1 and Fig. 2, and an increase in coefficient of expansion would result, thus checking Seger's findings.

Method D.—*Finer grinding of the quartz content.*

A comparison of curves 2 and 3 (Fig. 5) illustrates the operation of this method, and agrees with Seger's conclusion. Mention of this fact is made in discussing Fig. 5.

Method E.—*Harder biscuit firing.*

In my study no comparable data was obtained.

The data obtained agree with Seger's findings in every case where the materials used were similar to those with which he worked.

CONCLUSIONS.

I find that within the limits of this research the following statement holds:

The coefficient of expansion of the body is increased greatly by the substitution of flint for either feldspar or clay substance.

The coefficient of expansion of the body is not materially changed by substitution of feldspar for clay substance in the form of kaolin.

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The coefficient of expansion of the body is slightly increased by substituting clay substance in the form of ball clay for clay substance in the form of kaolin. The substitution of English china clay for kaolin apparently increases the coefficient of expansion of the body to a marked degree.

The coefficient of expansion of the body is increased very decidedly by substitution of finely ground flint for sand not so fine and which occurs in natural mixture with kaolin.

The coefficient of expansion of the body is not materially changed by substitution of pulverized calcined kaolin for flint provided that the kaolin is calcined at a temperature above that to which the body is fired.

DISCUSSION.

Mr. Weelans: What practical application has this to pottery in general?

Mr. Watts: I was investigating it with a view to some work in special electric porcelain pieces, where the coefficient seems to have a certain value.

Mr. Weelans: The reason that I asked is that the dunting proposition is interesting to potters, and we have never been able to determine its exact cause. We have often considered it as due to the varying coefficient of expansion.

Mr. Burt: The practical value of this proposition is that in a measure it is the power behind losses that we have, and this is the first time that we have taken the matter up scientifically. We have been groping in the dark and drawing hypotheses from results that we have not been able to check up from scientific determinations. We base our theories of craze, etc., on the coefficient of expansion, but we have never had any actual data on which to base our fundamental assumptions. If we can take our various mixtures, as I am delighted to see that Mr Purdy and Mr. Watts have done, and go through them, we can finally get to a point where we may, for instance, think that Mr. Stover is right in saying that crazing may not be due to

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difference in rates of expansion. The data will enable us to see whether one ingredient increases the coefficient or not.

Mr. Stover: I do not wish to be misunderstood as having said that it is not the coefficient of expansion that causes the shivering, for my thought was that in delayed cases the effect of the coefficient might be offset by that of elasticity. When two men like Mr. Purdy and Mr. Watts work on the same subject in different parts of the world and come to results so nearly alike, it makes us believe that there is something here that we must recognize.

Mr. Weelans: The subject of "dunting" we took up some time ago in a paper and gave three reasons for it, one was that defects in the wares themselves are largely responsible for it, composition of the mixture being only a part of the cause. We have often talked about the coefficient of expansion as applied to this defect, and it was easy for us to consider that this had something to do with the dunting. We are approaching the time when we shall know whether it has or not.

In our efforts to discover some of the causes of dunting our plan of procedure is as follows: We put a certain mixture into operation and note to what extent it is sensitive to this fault. When the ware is drawn, should there be any dunted pieces, they are broken, and frequently we find that the dunts started from some defect in the workmanship, such as hollow places, large and small, which are noticed in the pieces after breaking; again, parts of the ware are found to have opened as the seams, when not properly joined by the workmen, etc.

We are then about to say that defective workmanship alone is the fault—but we put other compositions into work and note that while the defects of construction mentioned still contribute to the dunting, it is also noticed that it appears in some compositions more than in others. It is, therefore, demonstrated that since some compositions dunt more than others, the fault is due to more than one cause.

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As the work progresses we try to determine which is the more satisfactory composition, and our attention is called to the fact that the higher the feldspar the more this trouble occurs. We are, therefore, persuaded to lower the feldspar as other body requirements will permit. It is this experience that has called forth our previous statement that "The higher the flint the less dunting we shall have, provided that we correspondingly increase the fire."

Now if we are firing a body which matures at cone seven and we increase the flint still continuing to fire it at cone seven, dunting will ensue; but it would not, in our opinion, be due to the increase of flint, but to the inadequate firing. for the body is now underfired. On the other hand, increase the flint and increase the temperature correspondingly and the dunting will be less than before, irrespective likewise of the defects in the body.

Therefore, we still maintain that the three faults which contribute most to dunting are:

1. Construction (joining the pieces together in the clay).
2. Composition.
3. Treatment.

In the manufacture of large pottery, dunting is all the time present. It is a serious problem.

Mr. Mayer: I want to give an emphatic amen to all that you have said, absolutely.

Mr. Maddock: Are you speaking of dunting in the biscuit or in the glaze?

Mr. Weelans: Either.

Mr. Stover: I think that we might look for some causes of dunting in our dry-rooms. You should not put green ware in the same room with pieces that are ready for the kiln. We are now working on a recording hygrometer by which we study the moisture conditions of our dry-rooms. When we get the record from the dry-room, we shall look to see why it is so and what the results will be.

Mr. Maddock: I would agree with Mr. Weelans,

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that you must increase the fire when you increase the flint. The reason that you have dunting in glost or biscuit is that the kiln is not fired high enough. If it is not fired properly, you will have twice as much dunting.

Mr. Watts: I should like to ask whether you find dunting in pieces of vitrified ware.

Mr. Weelans: Yes, sir, we do find loads of them.

Mr. Mayer: The reason that I spoke so emphatically in backing up what you said, Mr. Weelans, is that not only in England, but also in this country, dunting stops on the lines of which you spoke; but if you increase the flint and do not increase the fire, you are worse off than when you started.

NOTES PREPARED AFTER READING THE FOREGOING DISCUSSIONS.

Mr. Purdy: It may be well to review that which has been published in our Transactions on the subject of dunting before taking it up further. The supposed causes of dunting are listed here, with credit:

Hope,	p. 65, Vol. VIII	Too rapid cooling.
Weelans,	p. 81, Vol. VIII	Too rapid cooling.
Weelans,	p. 82, Vol. VIII	Overfire.
Weelans,	p. 83, Vol. VIII	Underfire.
Weelans,	p. 84, Vol. VIII	Unequal fusion.
Weelans,	p. 86, Vol. VIII	Defective construction.
Weelans,	p. 90, Vol. VIII	Too high content of feldspar.
Weelans,	p. 90, Vol. VIII	Lack of tensile strength in the clay.
W. D. Gates,	p. 96, Vol. VIII	Too rapid cooling.
Simcoe,	p. 349, Vol. XI	Pug mill laminations.
A. Mayer,	p. 295, Vol. XII	Too much non-plastic material.
A. Mayer,	p. 295, Vol. XII	Too rapid cooling.
Binns,	p. 302, Vol. XII	Too high content of quartz.
Ashley,	p. 302, Vol. XII	Lack of proper bonding material in the body.

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Ashley, p. 303, Vol. XII Strains set up by improper handling.

Stull, p. 303, Vol. XII Peculiar expansion of quartz.

Thomas, p. 305, Vol. XII Too close a grain.

A. There seems to be a unanimity on structural defects and too rapid cooling as the most frequent causes of dunting.

B. Mr. Weelans has not made plain in what way underfiring and overfiring of the ware produces, or even promotes dunting. From the testimony of Messrs. E. Mayer and J. Maddox there is danger in underfiring *only when the flint content of the body is too high*.

C. Want of tensile strength in the binding clay or too close a grain is productive of a weakness which I have often thought would follow from grinding the materials too fine, and for this reason I have thought it was fortunate for the potters that the clays they use are not more readily and completely disintegrated in the blunger, for if they were, the use of extremely fine flint and feldspar would cause the ware to be weak and punky, and very prone to dunt. Our students often overgrind their body mixes and get into these very troubles. The difficulties here are the same as those found by Professor Orton[1] when he attempted the use of too fine a sand or too "fat" a clay. I recently had a consulting experience with too thorough blunging of the body. A body blunged or treated with hot water until it gives difficulty in the filter press is very apt to produce unsound ware, an effect not always traceable to a separation of the body materials in the press.

Bedford shale, when ground in the dry pan and worked to a plastic condition in a pug mill, can be vitrified with safety, but when disintegrated in a blunger and filter-pressed, it is very prone to dunt if cooled too rapidly. I state this from sad experience. The reason? Primarily, too close a grain; secondly, defective structure caused

[1] Trans. A. C. S., Vol. 2, p. 100.

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by escaping moisture, combined water, etc.; and, thirdly, too tight a body to stand rapid cooling. I can believe that fusion need not progress beyond that necessary to produce a dense structure before annealing becomes a serious problem and that the coarser the material, the less need there is of annealing, no matter how thoroughly the mass is vitrified. Some of the terra cotta manufacturers know that this is too true.

D. I fail to follow Mr. Weelans in his argument that in underfired ware there is unequal fusion. His argument does not seem logical.

E. I can readily see that if the flint is increased, you must increase the heat if dunting is to be avoided. In fact, the reasoning underlying this is the same that prompted me to state (to Mr. Weelans) "That of the white ware ingredients, flint is the one most apt to provoke dunting. This is as Prof. Binns has stated the case, and is in agreement with the experience of E. Mayer and J. Maddox.

If the biscuit heat treatment is maintained the same, an increase in flint at the expense of feldspar will not only increase the proportional amount of material which fails to go into solution, thus decreasing the proportion of cementing bond which hardens the ware in the firing, but this increase in flint will also increase the proportional amount of the one constituent which, as Stull stated, suffers the greatest volume change when the ware is cooling. An increase in biscuit heat treatment will permit of increased solution of the flint, thus increasing the proportional amount of the cementing bond.

F. I can also see how it would be possible to have dunted ware with high feldspar and low flint even where care is taken in making and handling of the "green" ware, and in the cooling of the burned ware. If heavy ware is set in the kiln before being thoroughly dried, the dry portions of these large pieces will be heating up while the damp portions are drying out, thus permitting that which is dry to get considerably ahead in the process of vitri-

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fication. Orton and Griffen[1] have demonstrated this mathematically and they are frequently checked by observations in the burning of bricks. From paving brick experience, I would say that it is possible that this erstwhile damp portion may not attain the same degree of vitrification as the dry portion, and if it did attain an equivalent degree of vitrification, it would have a somewhat honeycombed structure, while the dried portion would be dense. It is not hard to see that if either of these conditions are attained, the body of the ware would be subjected to unequal strains when cooling, the resultant effect being a dunt. It is in this connection that I see occasion to apply Mr. Stover's suggestion that the cause of dunting may, in some cases, be traced to the drying room conditions.

G. A potter ran out of flint and credit at the one and same time, and having a stock of feldspar that felt like flint, he took a chance of using feldspar as a substitute for the flint. Of course he obtained a blue, vitrified biscuit on which his glaze could not do else than craze. We secured several of the 8-inch plates from this biscuit stock to use as tile setters in our experimental glaze burns. We invariably drew these kilns when so hot as to render asbestos gloves absolute necessities, and yet, these high feldspar and highly vitrified plates stood this sort of treatment repeatedly without dunting. One of these plates was on exhibition at the Trenton meeting of the Society. If Mr. Weelans' theories are wholly sound, why did these plates not dunt? They certainly had a high content of feldspar, were overfired and were refired several times.

Mr. Ogden biscuited his tile at cone 010 prior to taking them to Zanesville for burning in the large kilns, and every one of those which were highest in flint (and for that matter only those) dunted with glassy fracture even though cooled slowly. Mr. Weelans cites instances of this same sort himself when he says that refired biscuit invariably dunts.

[1] Page 9. "The Influence of Carbon in the Burning of Clay Ware," second report of Committee on Technical Investigation, N. B. M. A., Indianapolis, Ind.

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In summarizing, I claim that dunting follows from:

(1) Structural weakness in the clay state, such weakness being caused by:

(*a*) Too little bonding strength (Mayer).

(*b*) Improper handling (Ashley).

(*c*) Too close grain (Thomas).

(*d*) Pug mill or jigger laminations (Simcoe and Mayer).

(2) Structural rupture in the burned state caused by:

(*a*) Too rapid cooling (Weelans, Gates and others).

(*b*) Unequal vitrification or unequal structural density because of ware not being thoroughly dried.

(*c*) Too much flint, thus allowing within the vitrified mass too large a volume change in cooling (Stull).

I would imagine that the more flint there is in vitrified bodies, the more care would have to be exercised in cooling, and there would be less likelihood of successful refiring of the ware.

Let me repeat the contention which provoked this discussion from Mr. Weelans—of the materials used, flint is the most apt to produce dunting. In this, of course, I mean when used in excess of that required to produce vitrification under normal kiln conditions. My views of this dunting proposition are quite closely parallel with those of Arthur Mayer's.

I doubt if coefficient of expansion is a serious factor in the problem.

Mr. Burt: If Mr. Purdy would clearly define just what is meant by dunting, considerable confusion might be avoided. In my mind a dunt is a crack caused by sudden change of temperature acting on a body of high coefficient of expansion. It is practically the same phenomena as the breaking of a piece of cut glass when changed too quickly from hot to cold water; sudden high contraction on the surface while the main body has not contracted. In laboratory practice, we know that a jet of cold water, striking only a small part of a hot test tube, will probably break it, while if the whole tube is covered, no harm will be done. If, however, we are fortunate enough to possess

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silica glass tubes, the coefficient of which is low, they can be handled recklessly. So, contrary to Purdy, I hold coefficient is the main, if not the entire cause of dunt. When he talks of "structural weakness" and "structural rupture" in a burned state, he treats of an entirely different matter. It is here we need a definition of dunt. Cracks which may appear to be similar to dunt can often be traced to an original clay crack, others to a fire crack, but, to my mind, the true dunt comes to that otherwise perfect piece which, owing to its high coefficient, cannot accommodate itself to sudden temperature changes.

The question is: "What gives the high coefficient to the body?" Undoubtedly uncombined flint not only gives this high coefficient, but some investigators have shown that it is also an irregular coefficient. Purdy covers this under "E" and I agree with him here entirely, especially when he says: "An increase in biscuit heat will permit increase solution of the flint," but I would add to this, thereby changing from the high coefficient of the uncombined flint to the low coefficient of the combined.

Under "*G*" is cited a case of ware made from clay and feldspar, with no flint which failed to dunt. This confirms my theory, for with feldspar and clay (both with low coefficient) there is little chance for dunt. Flint, with its high coefficient is the real cause. Some ten years ago I wished to make dishes for boiling the sulphuric acid in rational analysis over a direct fire. It was evident that any regular high flint, non-vitrified white ware body would have high coefficient and dunt under the sudden temperature changes, so I made up a mix of 80 clay and 20 feldspar. Queer mix, I grant, but it worked to perfection. Another chance to test the theory was in the enclosing tubes for the pyrometer elements. Those supplied by the Berlin porcelain were not a porcelain but a porous, presumably, high flint body. These dunted on cooling with most distressing ease. It was evident I would have to make my own, so for these I tried a mix of 30 clay, 30 feldspar and 40 flint. Here is a high flint, why not a high coefficient

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and dunt? Simply because the body was fired to full vitrification and the uncombined high flint coefficient changed to combined flint of low coefficient. These tubes have given perfect satisfaction.

If a body has been so imperfectly made that distinct differences occur in its chemical or physical character, then it is easily conceivable that different coefficients may exist in the same body which might cause dunting. I claim, however, if this difference occurs in a majority of cases, trouble can be traced elsewhere and is not a true dunt. "Too little bonding strength, improper handling, too close (fine) grain, pug mill laminations" all cause clay to crack, a pure shrinkage problem often not to be seen until the ware is fired. The point is, certain mixes, no matter how perfectly made, will dunt, others will not. It is not a question of manipulation. It is a question of the coefficient of the perfectly made mix.

Mr. Purdy: Although differing in definition of dunting, Mr. Burt and I are in agreement as to the comparative influence of flint and feldspar in promoting the development of this defect, both of us differing from Mr. Weelans in opinion and experience in this.

I would refer Mr. Burt to a paper in this volume entitled "Chemical Porcelain," written by G. Murray, for an investigation of the very phenomena to which Mr. Burt would restrict the use of the term "dunt." Mr. Murray shows very distinctly that ability to stand sudden changes of temperature is not influenced much by composition of the body except in so far as structural density of the body is thereby likewise influenced, and that it was the more porous bodies rather than the most dense that stood the test.

Then, too, I would ask Mr. Burt to explain the sudden dunting of a large sanitary piece when in a stock room completely bathed in an atmosphere of equal temperature and which has not been subjected to sudden changes in temperature since having been drawn from the kiln.

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Mr. Weelans: Mr. Burt requests a clear definition of dunting. We explained in a previous note that dunting may appear in otherwise perfect ware, and also in ware of defective construction though the defects in construction would not, of themselves, destroy the ware, since dunts from one inch to a foot long often start from an infinitesimal small crack which crack would not at all, of itself, diminish the value of the piece, while the dunt completely destroys it. We term the fault a "dunt" despite its having started from a crack.

As previously explained by the writer, dunts emanating from cracks are, in a measure, increased or decreased according to the perfection or imperfection of the body composition.

Burt says dunts are a result of high coefficient of the body and that high coefficient of the body is due to high uncombined flint, while the writer gives, as his reason, "*underfire.*" This is a case of a distinction without a difference. If a high flint body be thoroughly vitrified it immediately loses its high coefficient because the flint is now combined, and, as a result of this combination, is of low coefficient, and of non-dunting character. In other words, it is now as the writer named it, a body of high flint fully combined, of low coefficient, thoroughly vitrified, and of low dunting ability. Yet, despite this, Prof. Purdy says, in his answer to Mr. Burt's note, that, "Although differing in definition of dunting, Mr. Burt and I are in agreement as to the comparative influence of flint and feldspar in promoting the development of this defect, both of us differing from Mr. Weelans in opinion and experience in this." To repeat, the writer gave as one cause of dunting, *underfire.* Is not a high *uncombined* flint body an underfired body? The writer gave as one help for dunting, "a high flint body thoroughly vitrified." What is this but a high combined flint, low coefficient, non-dunting body? On this, I quote Mr. Burt (in speaking of porcelain tubes for enclosing pyrometer elements): "Those supplied by the Berlin porcelain were *not porcelain* but a porous, presumably, high flint body. These dunted in cooling

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with most distressing ease." Mr. Burt presumes that this was a high flint porous body. I would also presume that it was, therefore, a porous high flint *underfired*, and, necessarily, a high coefficient and dunting body, which coincides exactly with our contention.

Quoting further from Mr. Burt's discussion: "It was evident I would have to make my own (meaning body), so for these I tried a mix of thirty clay, thirty feldspar, and forty flint. Here is high flint, why not a low coefficient and dunt? Simply because the body was fired to full vitrification and the *uncombined high flint coefficient changed* to combined and low coefficient. These tubes have given perfect satisfaction." In other words, a high flint and underfired body was a failure while a *fully fired* high flint body gave perfect satisfaction. This is exactly the argument used by the writer in his first note on the subject three years ago, and which he has ever since maintained.

Prof. Purdy, in the same discussion, refers Mr. Burt to a paper in this volume entitled "Chemical Porcelain," written by G. Murray. Prof. Purdy says that Mr. Murray shows very distinctly that ability to stand sudden changes of temperature *is not influenced much by composition* of the body except in so far as structural *density of the body is thereby likewise influenced*, and that it was more the porous bodies rather than the most dense ones that stood the test. Is not the openness and density of the body the cause of it all? We don't expect an open, high clay, porous body to dunt. The writer, in all his remarks upon the subject has repeatedly stated that the composition under discussion was a vitreous, close body, acceptable for heavy vitreous ware. One might ask, if clay does not dunt so readily and dunting is a trouble, why not increase the clay? I would answer by saying that a high clay body is not satisfactory in other ways; in fact, for the class of ware under discussion it is wholly impracticable. Surely no investigation was necessary to prove that an open body

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would admit of the exit of heat and entrance of cold more readily than a close, compact, vitreous body.

In a paper by the writer some time ago, we spoke of a *heavy grog vitreous* body which was used in some classes of ware where much greater thickness was desirable, the object of the incorporation of vitreous grog being to open the body, thus permitting it to be made in thicknesses much greater than was possible in regular vitreous. This open body, thoroughly vitreous, was filled with minute cells which permitted the heat of the body to be expelled so readily that the heated body in coming in contact with the cold failed to shatter or explode as would be the case with a fine, close grain vitreous body. This sort of body, however, could not be used in the finer grades of ware of which the writer has been discussing, owing to the fact that this incorporated vitreous grog gave it the appearance when broken of a rough and absorbent body.

Mr. Purdy asks an explanation for the "sudden dunting of large sanitary pieces when in the stock room, bathed as they are in an atmosphere of equal temperature." Our explanation for this, as given four years ago, is that on cooling the kiln this weakening action is first set up, and that it continues until the changing elements are stronger than the remaining strength of the piece, and that it is then that the dunt takes place.

The temperature in which the pieces are "bathed," however, is not so even as Prof. Purdy's remarks would indicate, for in winter, the stock room is often very cold at night but is warmed for the workmen during the day.

Mr. Burt: Mr. Murray's paper not having been published, I reserve comments on the conclusions Mr. Purdy says are given in it.

In regard to dunting of a sanitary piece in the stock room, I think this is a case not of dunting but of shivering that is, if same piece had no glaze trouble, dunting would not occur. As I have explained elsewhere, on cooling in the kiln, if glaze and body coefficients are not the same, a strain results, growing greater as the cooling advances.

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This strain may tend to craze or shiver as glaze contraction is greater or the reverse. Many pieces come from the kiln and go to stock room apparently perfect, but actually under a heavy strain. Some may not craze or shiver for years, if the strain is not very great. Just why elasticity should be sufficient to withstand this strain for a time and then fail, we do not know. A steel rail often becomes brittle in time under the blows from car wheels.[1]

Dunting is a different phenomena. Take a big piece of sanitary ware and allow it to cool properly, as it were, anneal it, the same will probably be perfect forever. Let it be a hurry job, send the kiln men into the kiln with gloves and draw this same piece hot out into cool air and you will not only see but hear the dunting.

Mr. Stover: Dunting undoubtedly has numerous causes as above explained, while some may originate and others may be increased in the dry room. In many dry rooms the degree of heat is the only factor considered and even this is under indifferent control, whereas the percentage of moisture is of equal, and, in many cases, of more importance in the accomplishment of safe and economical drying of ceramic wares of all kinds.

Experience has taught many of us that the dry rooms should be divided in separate sections, each section preferably having one or more kilns capacity. As each section is filled, the temperature should start low (about 70° F.); the humidity invariably should start high (96 to 98 per cent.), and as the heat is gradually increased the per cent. of humidity gradually lowered in proportion, thus avoiding surface checks or tension and allowing the internal moisture to travel by uniform capillary attraction to the surface without setting up unnatural strains or tensions which are frequently the original cause of ultimate dunting or, at least, which increase the tendency where other causes pre-exist.

The necessary apparatus is now available for auto-

[1] From crystallization (Ed.).

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matically controlling and continually recording the humidity and temperature. The records thus obtained are very useful for comparison and reference in perfecting and maintaining the best results in drying for the various forms of products.

Irregular dry room conditions have more to do in the production of dunting than is generally suspected.

Mr. Binns: I do not find in the foregoing discussion any mention of the change which is undergone by quartz or flint under high temperature or prolonged heating. I think this is an important factor and is partly responsible for changes in behavior. It is quite certain that quartz changes in form and finally loses altogether its crystalline structure when strongly heated. It may or may not enter into solution. The finer grains probably do but even the large and undissolved grains assume an amorphous form.

Mr. Purdy: I ask again that if given a "vitreous," close body acceptable for heavy vitreous ware in every case would Mr. Weelans have us believe that of the materials used, feldspar is the most apt to produce dunting?

I ask Mr. Weelans to again read the contribution by Watts, p. 185, Vol. XI, of our Transactions, entitled "Crystalline Structure in Porcelain" and then state if he still believes that in a vitrified body the flint is all in the amorphous state. I ask him further to prove that any of the flint is in the amorphous state, even in the most vitrified bodies. I have proof that it would likely be in the crystalline state though perhaps somewhat more subdivided.

Mr. Weelans: In answer to Prof. Purdy's question with reference to the possible state of flint in a vitrified body, would say that inasmuch as he himself is unable to make a positive statement in this connection (as the following sentence, quoted from Prof. Purdy, in speaking of flint in the body, will prove: "I have proof that it would *likely* be in the crystalline state, though perhaps somewhat more subdivided") it would be unwise for the writer,

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who has not had an opportunity to investigate this point as thoroughly as he would like, to do so. I take pleasure, however, in reiterating my former statement that high flint in a thoroughly vitrified body is as beneficial as high flint in an underfired body is dangerous.

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INFLUENCE OF CLAY, FELDSPAR AND FLINT ON COEFFICIENT OF EXPANSION OF CERTAIN WHITE WARE MIXTURES. BISCUITED AT CONE 10.

By Ross C. Purdy and Amos P. Potts.[1]

REVIEW OF PUBLISHED WORK OF OTHERS.

A most searching review of the literature on physics, physical chemistry, ceramics and allied subjects, shows that there is a conspicuous lack of data on this subject. It is true that a number of determinations of the coefficients of expansion of certain porcelains have been made, but in these cases no attention was paid to composition or constitution.

(1) T. G. Bedford read a paper on "The Expansion of Porcelain with Rise of Temperature" before Section A, of the British Association for the Advancement of Science, at Dover, in 1899, in which he quotes Deville and Troost (*Phil. Mag.*, Vol. 49, p. 91) as having determined the cubical coefficient of a sample of Bayeux porcelain, used in the air thermometer, as being 0.000,016 to 0.000,017. This determination was made by the usual dilatometer method. He also quotes from an article by German investigators, Holborn and Wien (*Ann. der Physik und Chemie*, Vol. 47, p. 107), who measured a piece of Berlin porcelain (composition unknown) 9 cm. long, at room temperature, and again at 500° and 1000° C., and came to the conclusion that the expansion was constant at 0.000,004 per unit length at 0° C.

(2) Bedford, in the same paper, gives an account of a determination of his own. He used a tube of glazed Bayeux porcelain about 1 meter long and 1.7 cm. in external diameter. Two fine transverse scratches ran around the tube at a distance of about 91 cm. from each other. Using a standard length, and a pair of reading microscopes, he directly compared the distance between these marks at a series of temperatures, ranging from 0° C. to 830° C.

[1] By permission of Dr. John A. Bownocker, Director Ohio Geological Survey.

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The microscopes were supported on solid stone blocks, resting on a solid stone bench, and could be moved along their slides by means of micrometer screws.

The tube was heated in a gas furnace, supported on a stand provided with leveling screws by means of which the marks were kept in focus.

The distance between two diamond marks on a glass tube, kept in a trough of melting ice, was used as a standard length. This distance equaled 91.394 cm.

As a result of this investigation he obtained the following expression: The length at a given temperature equals the length at zero centigrade multiplied by $(1 + 34.25 \times 10^{-7}t + 10.7 \times 10^{-10}t^2)$ which shows that the expansion is not a constant, but that the curve expressing elongation with rise of temperature is of the form $(ax^2 + bx + 1)K = y$, rather than $(ax + 1)K = y$, as had been assumed by Deville and Troost, and also by Holborn and Wien.

(3) On March 14, 1902, Mr. A. E. Tutton read, before the Physical Society, a paper entitled "The Thermal Expansion of Porcelain," which is published in *Phil. Mag.*, 6th Series, Vol. 3, No. 18, June, 1902.

His determinations were made on pieces of the same tube which had been used by Bedford and also by Chappius. His method was to use the interference dilatometer which he had previously described in *Phil. Trans.*, A, Vol. 91, p. 313, and Vol. 92, p. 455. For each determination, he used a piece of the tube 12 mm. long, and he worked over a temperature range from 10° to 120°.

Tutton's formula is similar to that of Bedford's except that his constants differ. As determined by Tutton the formula is $L_t = L_0(1 + (2522t + 7.43t^2)10^{-9})$.

(4) The formula as determined by Chappius and quoted by Tutton (the present writers have been unable to find a published account of Chappius's work) is $L_t = L_0(1 + (2824.1t + 6.17t^2)10^{-9})$.

(5) Tutton also quotes an article by Holborn and Day (*Ann. der Phys. und Chem.*, Vol. 2, p. 505, 1900) in which

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they state that between 250°–625° C. the formula for Berlin porcelain should be

$$L_t = L_0(1 + (2954t + 1.125t^2)10^{-9}).$$

(6) Mr. Watts, of the American Ceramic Society, published, in the *Trans. A. C. S.*, a paper on the coefficient of expansion as determined by him on a piece of porcelain of the type used in the manufacture of electric insulators at Victor, N. Y. His result, calculated by the straight line formula, gives as the coefficient of linear expansion for this particular porcelain 0.000,005,357.

(7) Dr. Mellor, in Vol. 5, *English Cer. Soc. Trans.*, describes a measurement of the coefficient of expansion of some English floor tile bodies. He found their coefficient to be 0.000,007,7 ±.

These several investigators and their results are here tabulated for ease of comparison:

Investigators	Temperature range	Formula. Used and linear coef. obtained	Cubical
Mellor	15°–100°	$L_t = L_0(1 + at) : a = 0.000,007,7$	
Deville and Troost	Not given	$L_t = L_0(1 + at) : a = 0.0000055$	0.000016 to 17
Watts	19°–243°	$L_t = L_0(1 + at) : a = 0.0000054$	
Holborn and Wien	0°–1500°	$L_t = L_0(1 + at) : a = 0.0000044$	
Bedford	0°– 830°	$L_t = L_0(1 + (3425t + 1.07t^2)10^{-9})$	
Chappius	0°– 83°	$L_t = L_0(1 + (2824t + 6.17t^2)10^{-9})$	
Holborn and Day	250°– 625°	$L_t = L_0(1 + (2954t + 1.125t^2)10^{-9})$	
Tutton	10°– 120°	$L_t = L_0(1 + (2522t + 7.43t^2)10^{-9})$	

We have, then, the result of eight independent investigations, four of which were made on Bayeux porcelain, and three of these on portions of the same tube. Of the other four, two were upon Berlin porcelain, the third upon a porcelain of the American insulator type, and the fourth upon an English floor tile body.

Aside from these investigations we find:

(8) Le Chatelier, H. "Sur la dilatation du quartz," *Bull. Soc. Min. de France*, Vol. XIII, pp. 112–118,

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Paris, 1890. (In connection with the expansion of clays upon burning.)

Coupeau, M. "Etude sur la dilatation des pâtes céramiques, III" *Bull. Soc. d'Encour.*, 97th year, Vol. III, 1274–1309 (Oct.), Paris, 1898.

(9) Vogt, Georges. "Observations deduites de l'étude sur les dilatations ceramiques de M. Coupeau," *Bull. Soc. d'Encour.*, 97th year, Vol. III, 1309–16 (Oct.), Paris, 1898.

(10) Granger, Albert. "Etude sur la dilatation des pâtes céramiques," *Moniteur scientifique*, Vol. LI, 385–392, Paris, 1899.

(11) Chantepie, M. "Sur la dilatation des pâtes céramiques," *Bull. Soc. d' Encour.*, 99th year, Vol. VI, 39-55, Paris, 1900. (Numerous diagrams and tables.)

Since the compositions of the porcelain used in these tests were not given, nor even available, they have but little bearing on the subject in hand.

VALUE OF SUCH DATA.

(1) The care which these investigators have exercised in their several methods to obtain accurate results has shown that they considered it very important to determine the coefficient of expansion of porcelain with a high degree of accuracy. In a majority of cases it was their intention to use the coefficient in the computation of temperatures by means of the air thermometer, for which purpose each was probably using a porcelain of the type examined. If it were of so great importance to know the coefficient of expansion of the particular type of porcelain which they were then using, of how much more importance is it to the manufacturer of scientific apparatus, if not to the scientist, to be able to appreciate the effect of variation in his body mix?

(2) But there is a second, and it would appear from a purely ceramic standpoint as a more important reason for the investigation of this matter, and that is the obtaining

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of data bearing on the fundamental assumptions on which many of our theories are based.

In Vol. II, p. 572, of "Seger's Collected Writings," we find this statement: "The principal difficulties which arise in the production of a faultless union of body and glaze lie in the different expansions which these experience, when subjected to heat." From this assumption, Seger formulated a set of rules for controlling glaze fit. As a matter of fact, his rules are workable in some particular cases, but there is no proof of the validity of his fundamental assumptions. Furthermore, it has not been shown that his rules could be used in the manufacture of porcelain for scientific apparatus where low coefficient of expansion of the porcelain is a desideratum.

For a number of years, Mr. Stanley G. Burt investigated the effect of the body ingredients, particularly silica, upon glaze fit.[1] In the first two of these papers, he devotes most of his attention to flint—its origin, size of grain, etc., but in the last paper, he offers a series of what he calls "Coefficient Equivalents." He expressly states that these are arbitrary figures based upon his own experience. We will not, at this time, take issue with him as to the value of these figures for controlling glaze fit, but we raise a question concerning their value as *Coefficient of Expansion Equivalents*.

Is Seger's assumption correct? Is glaze fit a function of the relative coefficient of expansion of the body and glaze? As an aid in formulating working theories, an investigation of the fundamental assumptions is eminently worth the while.

THE PRESENT INVESTIGATION.

The bodies used are the same as those described by Ogden.[2]

Making the Trial Pieces.—The trial pieces for the

[1] Trans. A. C. S., Vol. 3, p. 18; Vol. 5, p. 340; and Vol. 7, p. 133.
[2] Page 394, this volume.

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expansion tests were pressed by hand into plaster moulds. In shape, they were rectangular, being 5″ long, 3/4″ wide, and 3/8″ thick.

Burning.—The trials were placed in saggars and fired with coke for 40 hours until cone 10 heat treatment was obtained. In placing the trials in the saggars, the expansion trials were laid lengthwise on a cushion of sand to prevent them from warping or bowing.

Description of Apparatus First Used.[1]—In the preliminary tests the following apparatus was used to determine the expansion of the trials.

Upon a triangular brass bar were mounted two microscope holders, which could be moved backward and forward along the bar under control of slow motion screws. In these holders were placed two microscopes each fitted with micrometers. In the microscopic field on each microscope were two horizontal parallel cross-hairs, one of which was stationary and the other controlled in movement by the micrometer wheel.

Heating of Trials.—It was decided to heat the trials by submerging them in an oil bath. For this purpose a bath tank was constructed of copper-tin, the tin being on the inside as it was less liable to the oxidation effects of the oil at high temperatures. The dimensions of the tank were 6″ in length, 3″ in width, and 2 1/2″ deep.

At first it was planned to heat the oil by a resistance coil, but this proved inadvisable on account of the unequal heating of the bath. Finally a resistance pad of asbestos wound with No. 28 Climax wire was tried and found to work most satisfactorily.

The following photograph is a view of the complete apparatus.

The space between the tank and the supporting bar was filled with a sheet of asbestos to prevent heat from causing expansion of the bar. Small holes were left in this packing to allow a sight on the trial piece.

[1] This preliminary work was done by Karl Meuche as a thesis under the direction of the senior writer.

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Choice of Oil for the Bath.—This afforded considerable trouble as the bath had to be a transparent one and remain so at the maximum temperatures used in the test. It also had to have a boiling point higher than the temperatures at which the expansion was to be determined. Lard oil, paraffine oil and olive oil were subjected to preliminary tests and, while transparent, were found to discolor at high heats and lose their transparency. Glycerine was then

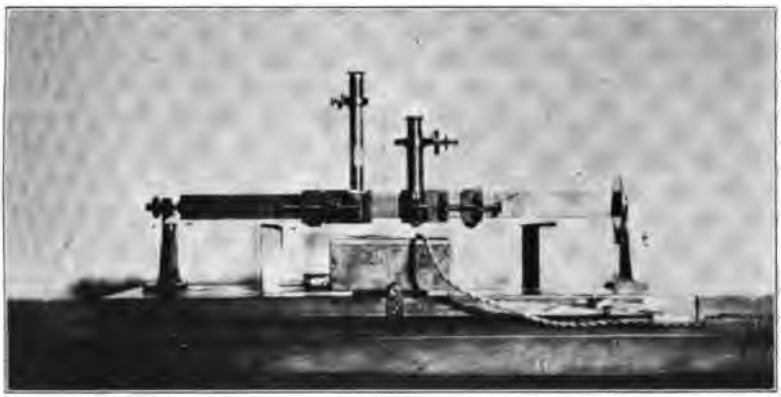

Fig. 1.—View showing rear of apparatus with tank.

tried and found very satisfactory, with the exception that it fumed at 150° C., clouding the lens of the microscope, thus dimming the focus.

Calculations.—The coefficient of expansion was figured from the formula

$$L = \frac{L_2 - L_1}{L_1(t_2 - t_1)},$$

where

L_2 = heated length in millimeters,
L_1 = original length in millimeters,
$(t_2 - t_1)$ = temperature range.

The Method Finally Adopted.—There are many faults in the method just described but the one which really

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caused its abandonment was the limited heat range. We were unable to find a transparent oil which would remain fluid over a range of more than 180° C. and as it was desired to extend our readings to 500° C., we had to resort to the use of a small electric furnace.

As finally constructed, the furnace was an oblong box, built of 1/8″ asbestos lumber, and lined to a thickness of 3/4″ with a mixture of oxychloride cement and asbestos. The inside dimensions of this box are 1 1/2″ x 2″ x 6″. In the bottom of this box were placed the five heating coils, evenly spaced. Each coil consisted of about 12″ of doubled and twisted No. 28 Climax wire, wound on biscuit porcelain blocks, 1″ x 1 1/2″ x 1/8″, the wire being held in grooves on the blocks by means of a pair of similar porcelain blocks which were fastened one to each side of the core.

These five coils, connected in series, were sufficient to give a temperature in the furnace of 600° C. in about one and a half hours, with alternating current at 110 volts and 3 amperes, but if heated continuously much above 500° C., the coils would quickly burn out; hence, no measurements above 500° C. were attempted.

The coils being placed, the whole box was covered with a flat lid consisting of three layers of 1/8″ asbestos lumber, firmly fastened together. In this cover were two window spaces, 1 1/2″ square, and spaced about 4″ from center to center. These window spaces were covered with two thin sheets of mica, each fastened on either side of the middle layer of the asbestos cover.

To facilitate focusing, the furnace rested upon an asbestos platform, supported upon three leveling screws.

In series with the heating coils was a Thomson ammeter and a bank of lamps in parallel as external resistance.

In place of having two microscopes with movable cross-hairs, only one was used, the other microscope having fixed cross-hairs and no vernier. This simplified the recording of the data, for with the two verniers, it was always

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necessary to record the direction as well as the number of divisions turned.

The rods carrying the microscopes were clamped to a horizontal rod in a horizontal position but at right angles to it. In this way the heat radiated from the furnace expanded the two rods, carrying the microscope farther from the first horizontal rod but did not alter the distance between them. The first horizontal rod and the upright carrying it were protected from these radiations by a large sheet of asbestos lumber placed vertically about midway between them and the furnace.

Calibrating the Micrometer.—To calibrate the micrometer, we used a brass standard meter bar graduated to millimeters and correct at 15° C. The number of divisions necessary to carry the cross-hairs from one side of one millimeter division to the corresponding side of the next were counted, being careful to always turn the micrometer in the same direction to avoid the back lash in the micrometer screw.

The first five counts were as follows:

Initial reading of micrometer.....	27	20.7	21	23.7	23.0
Final reading of micrometer.....	776	772.3	769	768.0	770.5
Divisions turned.....	749	751.6	748	747.3	747.5

The meter bar was then shifted and a second division measured to eliminate the error in marking the meter-bar. These results follow:

Initial reading.....	18	16.3	16	17.7	16
Final reading.....	783	781.0	780	783.0	780
Divisions turned.....	765	764.7	764	765.3	764

These ten measurements were then averaged, giving 756.6 as the number of divisions equivalent to the distance between the millimeter division.

As the meter-bar is correct only at 15° C., and the readings were made at 28° C., a correction for temperature had to be made. This would make the distance between the millimeter divisions at 28° C. equal 1.000,244,4

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mm. This quantity divided by the mean number of turns as above obtained makes each division equal to 0.001,322 mm. No correction was made for the expansion of the micrometer screw as it is also of brass and would probably expand the same as the meter-bar.

Had the correction for temperature for the meter-bar not been made, the value of one division would have been 0.001,321,7, a difference of 3 in the seventh decimal place for a range of 13° C.; hence, the value for the micrometer divisions was not calculated for each of the temperatures at which measurements were made.

A thermometer, suspended with the bulb just on a level with the object glass of the microscope when the temperature of the furnace was 500° C. and the room temperature 32° C., registered 44° C. The same thermometer, when suspended with the bulb just touching the micrometer cases and the furnace still at 500° C., registered 35.5° C. If the mean of these temperatures is taken, the correction of the micrometer should be for 25° C. instead of 13° C., as shown above. This would give a value of 0.001,322,3 for each division on the micrometer head.

SOURCE OF ERROR AND ATTEMPT TO OBVIATE THE SAME.

We were cognizant of several sources of error and attempted to obviate some of them. Some of the sources of error, which, because of their irregularity, cannot be allowed for in computation, are as follows:

Unequal Heating of the Test Piece.—On finding that the heat distribution did not vary more than 0.1° C. in any part of the furnace, the trial piece was held at the required temperature until no further elongation could be observed.

Expansion of the Bars which Supported the Microscopes.—This was, so far as could be determined, obviated by heat shields.

Back-lash in the Micrometer Screws.—This was ob-

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viated by always turning the screw in the same direction when bringing the cross-hairs into position.

Errors in Measurement.—The marks on the trials, although made with a sharp steel point, were so wide that it was impossible to use them; hence, the microscopes were originally set with their field cross-hairs exactly 8 cm. apart. Small black dots in the lines made by the steel point were then so selected that a dot on one end of the tile was in an angle of the fixed cross-hairs and separated therefrom by a hair line of white; the other selected dot at the other end of the tile was similarly situated with regard to the movable cross-hairs when their intersection coincided with the vertical fixed cross-hairs of that microscope. These dots were then identified by their position relative to those of the more conspicuous dots. The only error thus introduced was in estimating the width of the hair line of white between the dot and cross-hair, but this could not be avoided and was found to be much less than the error introduced when the dot was allowed to touch or coincide with the cross-hairs.

Irregularity in the Observed Temperature.—Inasmuch as we made the reading at 100, 200, 300, 400 and 500° C., we had to use a thermocouple and galvanometer, and as the divisions on the galvanometer were rather large, an error of 5° C. may have been introduced in each of the observations. But as the current was nearly constant and to insure equal heating of the test pieces, the temperature had to be held over long periods of time, it is hardly probable that the error ever reached this limit.

Unequal Structure in the Trial Pieces.—It will be remembered that all of the trial pieces were made by being pressed by hand into plaster moulds. This method does not produce a uniform structure throughout the series, for the operator unconsciously treats each mixture according to its texture. Besides, hand-pressing of brickettes always produces structural defects.

It is proposed that in further work, a uniform struc-

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ture in the trials will be approximated by casting the clay on a plaster slab, cutting the brickettes with a cutter similar to a cake cutter, and then pressing them under a uniform constant pressure by a method similar to that used in making brickettes for tensile strength tests.[1] It is also purposed to make the brickettes 25.0 cm. instead of 8 cm. long in order to reduce the accumulated error due to all sources.

DATA OBTAINED.

The coefficients here given are not offered as the exact coefficients for these body mixtures, for while the micrometer was accurately calibrated, in none of the readings was any attempt made to interpolate between divisions and in making the measurements, three check readings within one division were taken as final, so that so far as the real coefficient is concerned some error may have thus been introduced. However, it is believed that the results are relative and that they are valuable in discussing the subject in hand. Furthermore, considerable dependence can be placed in the actual values for the tests were repeated three times in all cases and in several, four and five times.

The data obtained are assembled in the following tables:

[1] Bull. 9, Illinois Geol. Surv., p. 163.

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Original length, 80 mm. Each division turned = 0.001322 mm.

		100° C			200° C		300° C		400° C		500° C	
	Brickette No.	Room temp.	Temp. range	Coefficient	Temp. range	Coefficient	Temp. range	Coefficient	Temp. range	Coefficient	Temp. range	Coefficient
Series V	1	27	73	0.06338	173	0.06591	273	0.06295	373	0.06590	473	0.06533
	2	25	75	0.05288	175	0.05571	275	0.05283	375	0.05332	475	0.05323
	3	25	75	0.06610	175	0.06886	275	0.06730	375	0.06678	475	0.06749
	4	27	73	0.06338	173	0.06304	273	0.06416	373	0.06335	473	0.06323
	5	27	73	0.06338	173	0.06400	273	0.06416	373	0.06379	473	0.06393
	6	28	72	0.06656	172	0.06629	272	0.06618	372	0.06663	472	0.06617
	7	20	80	0.06817	180	0.06763	280	0.06787	380	0.06784	480	0.06747
	8	23	77	0.07082	177	0.07095	277	0.07099	377	0.07057	477	0.07067
	9	23	77	0.07313	177	0.07188	277	0.07158	377	0.07187	477	0.07176
Series W	1	25	75	0.06390	175	0.06421	275	0.06310	375	0.06346	475	0.06332
	2	23	77	0.06438	177	0.06535	277	0.06622	377	0.06571	477	0.06548
	3	22	78	0.06459	178	0.06357	278	0.06329	378	0.06316	478	0.06273
	4	23	73	0.06241	173	0.06178	273	0.06235	373	0.06247	473	0.06254
	5	23	77	0.06009	177	0.06442	277	0.06025	377	0.05907	477	0.06029
	6	23	77	0.06224	177	0.06018	277	0.06025	377	0.06049	477	0.06029
	7	25	75	0.06610	175	0.06610	275	0.06610	375	0.06610	475	0.06610
	8	27	73	0.06928	173	0.07068	273	0.07082	373	0.07082	473	0.07090
	9	29	71	0.07215	171	0.07150	271	0.07195	371	0.07126	471	0.07192
Series X	1	26	74	0.05806	174	0.05698	274	0.05729	374	0.05744	474	0.05752
	2	25	75	0.05288	175	0.06222	275	0.06009	375	0.05993	475	0.06018
	3	26	74	0.05582	174	0.06077	274	0.05850	374	0.05832	474	0.05859
	4	26	74	0.05806	174	0.05698	274	0.05789	374	0.05788	474	0.05787
	5	26	74	0.06476	174	0.06363	274	0.06333	374	0.06363	474	0.06380
	6	22	78	0.05508	178	0.05570	278	0.05573	378	0.05508	478	0.05558
	7	22	78	0.06144	178	0.06313	278	0.06301	378	0.06295	478	0.06290
	8	23	77	0.06653	177	0.06628	277	0.06622	377	0.06662	477	0.06651
	9	27	73	0.07244	173	0.07165	273	0.07082	373	0.07088	473	0.07119

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Original length, 80 mm.					Each division turned = 0.001322 mm.							
		100° C			200° C		300° C		400° C		500° C	
	Brickette No.	Room temp.	Temp. range	Coefficient	Temp. range	Coefficient	Temp. range	Coefficient	Temp. range	Coefficient	Temp. range	Coefficient
Series V	1	25	75	0.04627	175	0.04721	275	0.04627	375	0.04627	475	0.04627
	2	22	78	0.04449	178	0.04558	278	0.04518	378	0.04547	478	0.04529
	3	25	75	0.04406	175	0.04435	275	0.04387	375	0.04406	475	0.04418
	4	23	77	0.04721	177	0.04668	277	0.04936	377	0.04646	477	0.04732
	5	24	76	0.05217	176	0.05258	276	0.05209	376	0.05230	476	0.05242
	6	25	75	0.05510	175	0.05680	275	0.05588	375	0.05597	475	0.05566
	7	23	77	0.05365	177	0.05508	277	0.05429	377	0.05435	477	0.05439
	8	25	75	0.05723	175	0.05760	275	0.05709	375	0.05729	475	0.05740
	9	26	74	0.06700	174	0.06743	274	0.06694	374	0.06672	474	0.06700
Series Z	1	26	74	0.04689	174	0.04747	274	0.04704	374	0.04728	474	0.04706
	2	25	75	0.06389	175	0.06232	275	0.06268	375	0.06346	475	0.06332
	3	26	74	0.05806	174	0.05793	274	0.05789	374	0.05744	474	0.05752
	4	26	74	0.04913	174	0.04938	271	0.04945	374	0.04949	474	0.04951
	5	26	74	0.04019	174	0.04084	274	0.04087	374	0.04021	474	0.04097
	6	27	73	0.05429	173	0.05349	273	0.05326	373	0.05360	473	0.05380
	7	23	77	0.05794	177	0.05975	277	0.05787	373	0.05742	477	0.05785
	8	25	75	0.05728	175	0.05949	275	0.05703	375	0.05729	475	...
	9	26	74	0.04913	174	0.04938	274	0.04885	374	0.04904	474	0.04913
Series A	1					See V 1						
	2	25	75	0.07051	175	0.06988	275	0.06971	375	0.06963	475	0.06958
	3	28	72	0.06426	172	0.06533	272	0.06500	372	0.06530	472	0.06512
	4	28	72	0.06426	172	0.06437	272	0.06440	372	0.06441	472	0.06476
	5					See W 5						
	6	30	70	0.05366	170	0.05903	270	0.05880	370	0.05850	470	0.05907
	7	27	73	0.06620	173	0.06759	273	0.06659	373	0.06723	473	0.06743
	8	28	72	0.07115	172	0.07109	272	0.07108	372	0.07107	472	0.07142
	9					See X 9						

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Original length, 80 mm. Each division turned = 0.001322 mm.

		100° C			200° C		300° C		400° C		500° C	
	Brickette No.	Room temp.	Temp. range	Coefficient × 10^{-4}	Temp. range	Coefficient × 10^{-4}	Temp. range	Coefficient × 10^{-4}	Temp. range	Coefficient × 10^{-4}	Temp. range	Coefficient × 10^{-4}
Series B	1					See W 1						
	2	30	70	0.06610	170	0.06610	270	0.06610	370	0.06387	470	0.06504
	3	26	74	0.06030	174	0.05983	274	0.05971	374	0.05965	474	0.05926
	4	26	74	0.05888	174	0.05699	274	0.05730	374	0.05744	474	0.05752
	5	23	77	0.05780	177	0.05788	277	0.05787	377	0.05753	477	0.05785
	6	24	76	0.05217	176	0.05539	276	0.05628	376	0.05669	476	0.05696
	7	27	74	0.04913	174	0.05390	274	0.05488	374	0.05523	474	0.05578
	8	25	75	0.04846	175	0.05265	275	0.05283	375	0.05288	475	0.05323
	9					See Z 9						
Series C	1					See X 1						
	2	28	72	0.05736	172	0.05801	272	0.05772	372	0.05775	472	0.05734
	3					See Y 3						
	4	25	75	0.04186	175	0.04155	275	0.04206	375	0.04186	475	0.04209
	5					See Z 5						
	6	26	74	0.06253	174	0.06268	274	0.06212	374	0.06274	474	0.06240
	7	28	72	0.06885	172	0.06725	272	0.06926	372	0.06885	472	0.06862
	8	27	73	0.07017	173	0.06973	273	0.06901	373	0.06911	473	0.06917
	9	27	73	0.06791	173	0.06782	273	0.06779	373	0.06734	473	0.06748
Series D	1					See Y 1						
	2	29	71	0.05819	171	0.05895	271	0.05793	371	0.05790	471	0.05799
	3	29	71	0.06051	171	0.05992	271	0.05976	371	0.05790	471	0.05939
	4	27	73	0.06338	173	0.06400	273	0.06416	373	0.06380	473	0.06393
	5	28	72	0.06885	172	0.06821	272	0.06809	372	0.06797	472	0.06748
	6	28	72	0.06197	172	0.06245	272	0.06192	372	0.06219	472	0.06232
	7	26	74	0.06476	174	0.06363	274	0.06332	374	0.06362	474	0.06356
	8	24	76	0.06958	176	0.06948	276	0.06945	376	0.06945	476	0.06943
	9	26	74	0.07146	174	0.07123	274	0.07117	374	0.07158	474	0.07199

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The values for "Elongation" were obtained by multiplying "Divisions Turned" by the value of each division.

The values in the column headed "Coefficient Linear 10^{-4}" are obtained from the following equation,

$$\frac{E}{L \times t} = C,$$

where

E = elongation,
L = 80 mm., the length at initial temperature,
t = temperature range,
C = the mean coefficient thus obtained.

To economize space in the table, this coefficient has been multiplied by 10,000.

To assist in interpreting this data, a plaster model was made (Fig. 2). A triaxial diagram was first laid out on a level table top and the bodies located thereon. At each point, representing a body mixture, a hole was bored into which was fitted a wooden peg. These pegs were cut in lengths proportional to the coefficient of the body represented. In order that the model might not be inordinately high, a flat cut of three inches was made on each peg.

The method of finding the proper length of peg to represent Body V 9, for illustration, whose coefficient of expansion is 0.000,007,2, is as follows:

$$0.000,007,2 \times 1,000,000.0'' = 7.2''.$$
$$7.2'' - 3'' = 4.2''.$$

The peg would be cut to such a length that when driven into the table, it would project 4.2″ above the surface.

When all the pegs had been driven, the space between them was filled with clay and the clay worked down to a smooth surface just touching the tops of the various pegs. From this, a plaster model was cast.

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DISCUSSION OF DATA.

General Observations.

(1) The contour of the model is not a plain, as one would be led to expect from Burt's expansion equivalents.

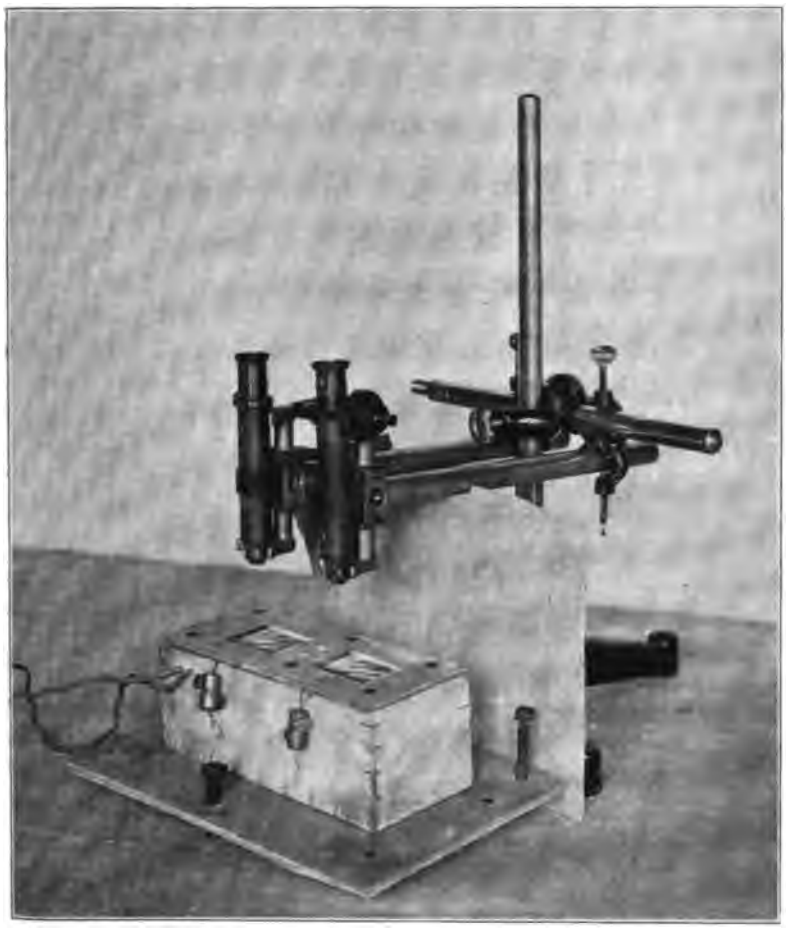

Fig. 2.

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(2) The body having the lowest coefficient is not the one containing the most clay or the most feldspar as would be expected from Seger's Laws.

(3) The body containing 50 per cent. feldspar has nearly as great a coefficient as has the body containing 70 per cent. of flint, the coefficient being 0.000,007,1 and 0.000,007,2 respectively.

(4) Probably the most striking feature of the whole model is the relatively low coefficient of all the bodies containing between 25 per cent. to 30 per cent. of feldspar.

(5) The minimum coefficient found in this study was that of the body containing 30 per cent. feldspar, 30 per cent. flint and 40 per cent. clay. In the immediate neighborhood of this body there were five others, the coefficients of expansion of which were nearly as low.

Discussion of Data in Reference to Seger's Laws.—We take it that Seger's laws, derived from experiments with white ware bodies, are not to be expected to apply much outside of the area of practical white ware body compositions, *i. e.*, 8–20 per cent. feldspar, 40–52 per cent. clay, and 28–52 per cent. flint.

(1) Within these limits, when flint is less than 45 per cent., we find that with any mixture of flint and feldspar, or even when added at the expense of flint—clay slightly *increases* rather than decreases the coefficient of expansion. But even though clay does increase the coefficient, it will also cause crazing.[1]

(2) While maintaining flint constant, addition of clay at the expense of feldspar, within these limits, also increases the coefficient, but does not materially affect the glaze fit, *i. e.*, if there is perfect accord between the body and glaze, it will not be jeopardized by substituting clay for feldspar, provided always that the total flint content is not altered. Yet such substitution would cause an increase in the coefficient of expansion.

(3) Upon adding feldspar to any given ratio of flint

[1] See p. 576, Vol. II, Seger's Collected Writings.

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to clay, within these same limits, or keeping clay constant and adding feldspar at the expense of flint, decreases the coefficient and carries us from the area of fit to that of crazing. This is as Seger thought.

(4) Flint (up to 45 per cent.) added to any given ratio of clay to feldspar within these same limits, or when substituted for clay, while maintaining feldspar constant, slightly *decreases* the coefficient and at the same time carries us from the area of crazing into fit; while if clay is maintained constant and flint is substituted for feldspar, the coefficient is *increased*, and at the same time the tendency to craze is overcome.

(5) We find then that the bodies within this limited area (the area of practical pottery bodies), feldspar is most active in reducing the coefficient of expansion, and the clay the most active in raising it, while flint seems to have but slight effect one way or the other, until it exceeds 50 per cent. of the total batch.

(6) Seger says ("Seger's Collected Writings," Vol. II, p. 576): "By increasing the clay bonding material in a body, the expansion of the same with a rise of temperature is decreased." This we have not found to be true, if this statement meant that the clay is to be added to an already satisfactory body in amounts only sufficient to cause crazing. It is true only after the total clay content exceeds 55 per cent. of the batch.

(7) Again, on the same page, we find the statement that "An increase of feldspar (constant ratio of clay to quartz), therefore, acts also in direction of reducing the expansion or contraction of the body of the ware." This is clearly demonstrated by our data.

(8) In reference to flint (quartz), Seger says: "By raising the content of quartz, the coefficient of expansion of the body is raised." We have not found this to be true within practical working limits, but it undoubtedly is true after the flint has become 50 per cent. or more of the mix.

(9) It may be said then that starting with a practical

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working body and keeping within practical working limits, our data supports Seger's hypothesis only in one instance, *i. e.*, feldspar does decrease the coefficient of expansion. Within these limits, however, clay increases while flint slightly diminishes the coefficient, effects quite contrary to what Seger supposed.

(10) Examining the coefficient along the craze line as determined by Dr. Hecht, we find the following bodies situated on each side of the craze line:

Crazed body coefficient		Fit body coefficient	
W-1	0.0000064	V-2	0.0000053
B-2	0.0000066	A-2	0.0000069
Y-2	0.0000060	W-3	0.0000063
C-3	0.0000044	B-3	0.0000060
Y-3	0.0000044	X-3	0.0000058
Z-3	0.0000058	C-4	0.0000042
D-3	0.000060	Y-4	0.0000047

It will be seen that three of the seven bodies in the above table, under the heading "Crazed," have a higher coefficient than the bodies in the corresponding series which lie within the area of "Fit," also body Z-9, containing 30 per cent. feldspar, 20 per cent. clay and 50 per cent. flint, is on the opposite side of the diagram from where crazing is to be expected and has a coefficient of only 0.000,004,9, or less than most of those listed above as "Crazed."

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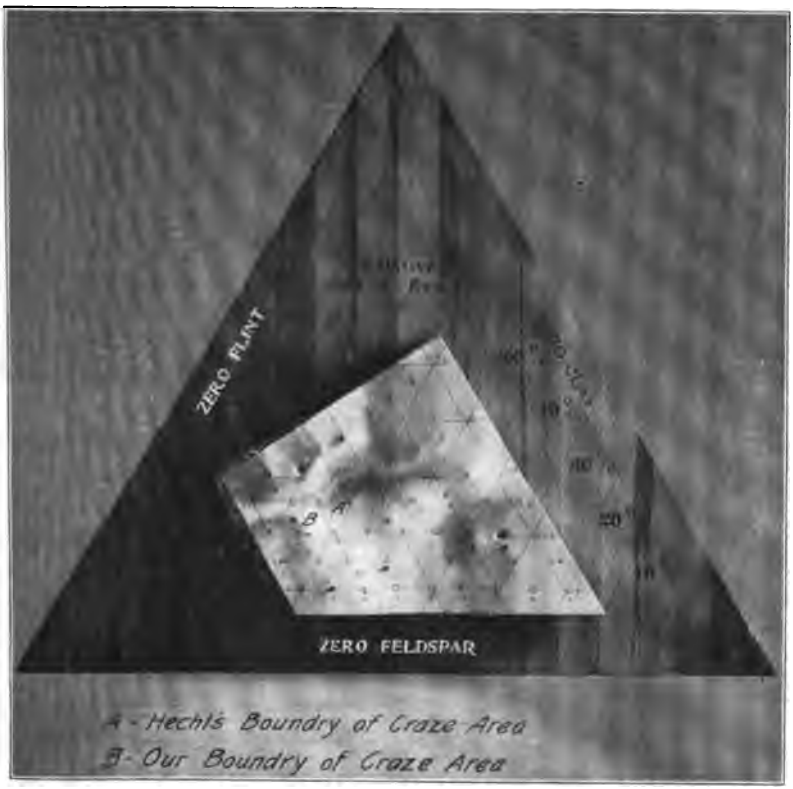

Fig 3.

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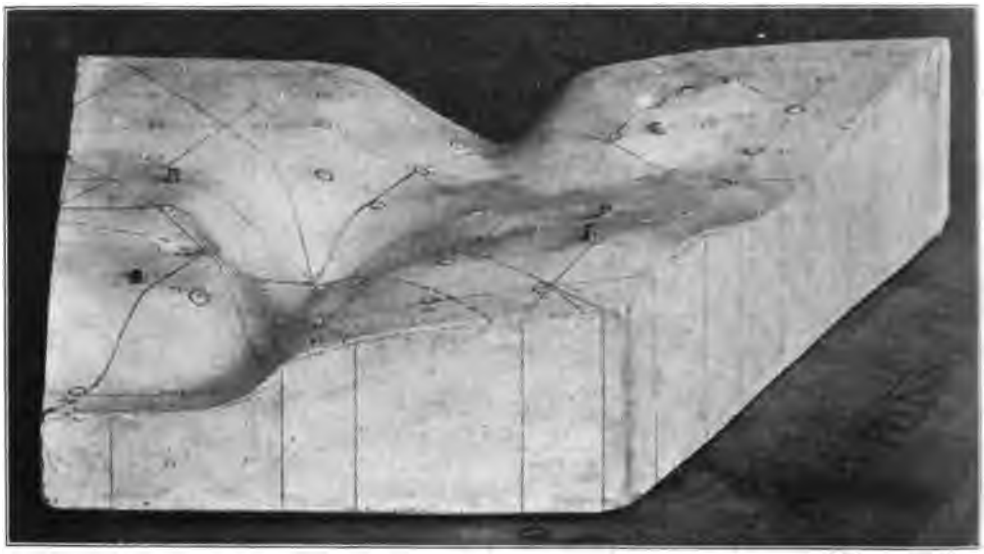

Fig. 3*a*.

Discussing of Data in Reference to the Whole Field.

(1) Starting with the body having the lowest coefficient of expansion (30 per cent. each of flint and feldspar and 40 per cent. of clay) and noting the effect of increase of flint, keeping the feldspar and clay always in the same proportion, we find:

(*a*) The first 5 per cent. addition of flint causes an abrupt rise in coefficient from 0.000,004,1 to 0.000,005,2.

(*b*) With the next 5 per cent. addition of flint, the increase in coefficient continues, but less abruptly.

(*c*) With a further addition of 5 per cent. of flint to this minimum coefficient body, making a total of 45 per cent. flint, we find a slight decrease.

(*d*) But with further addition of flint (from 45 to 60 per cent.) we find there is a comparatively large increase in coefficient.

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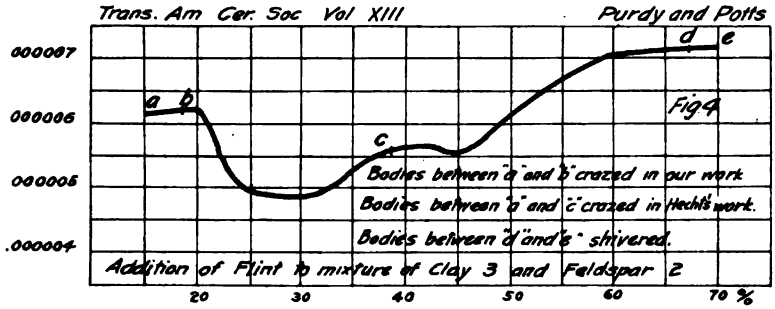
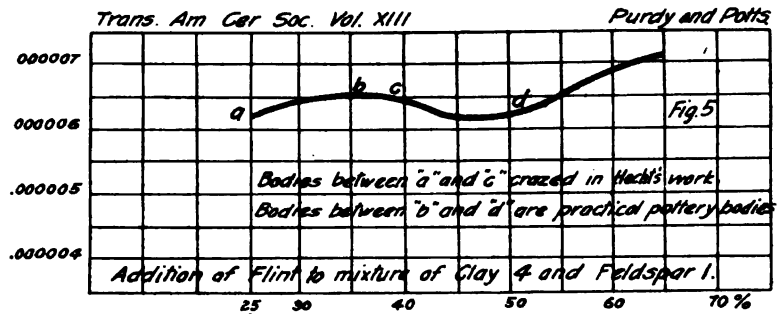
The history of an effect of flint similar to this is shown in Fig. 4.



(2) The effect of addition of flint to a mixture of 4 of clay and 1 of feldspar is to be seen in Fig. 5.

When flint is 40 per cent., the clay and feldspar would be 48 and 12 per cent., respectively. It is to be noted, therefore, that this curve passes through the middle of the area of practical pottery bodies.



(3) The effect of addition of flint to a mixture of clay and feldspar in equal proportion is traced in Fig. 6.

(4) The effect of addition of flint to a mixture of 7 of clay and 3 of feldspar is shown in Fig. 7.

(5) The highest coefficient of expansion was obtained with the highest content of flint and with it shivering of the glaze occurred. This is in harmony with Seger's views.

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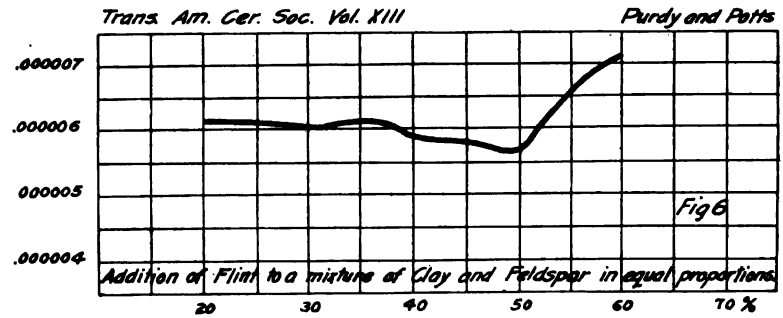
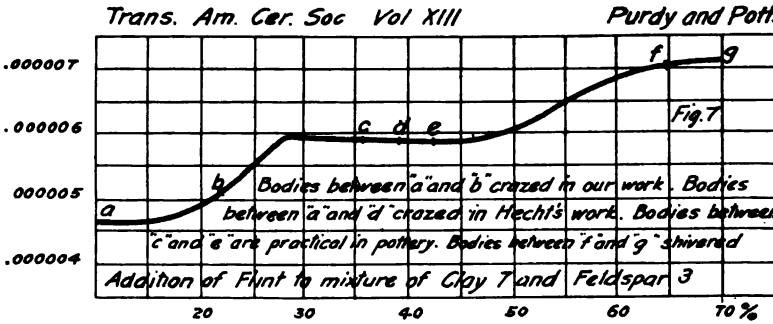
But, additions of flint did not, at all times, increase the coefficient of expansion, nor can the ability of a given glaze to stand without crazing be attributed to any particular coefficient of expansion of the body.



(6) Neither Hecht nor we found crazing on the body which, in this study, has the lowest coefficient of expansion, while several bodies with a much higher coefficient did cause crazing.



(7) Furthermore, with flint constant at 30 per cent. we find the coefficient varying with variations in proportion of clay to feldspar (as traced in Fig. 8) much more abruptly than it did with variations in content of flint.

(8) With flint constant at 40 per cent. we find the effect of variation in clay and feldspar as is traced in Fig. 9.

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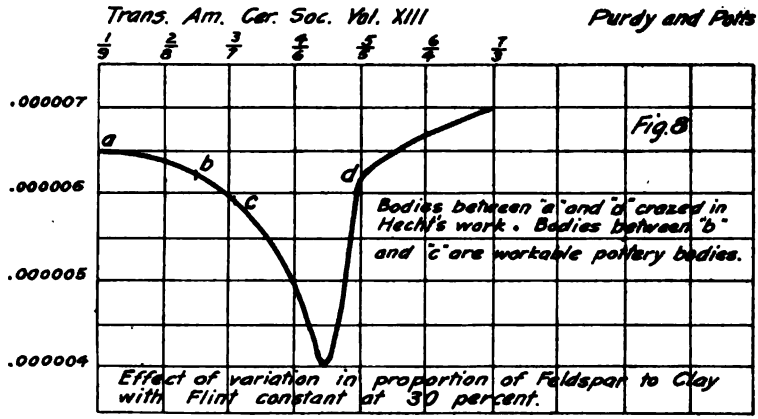
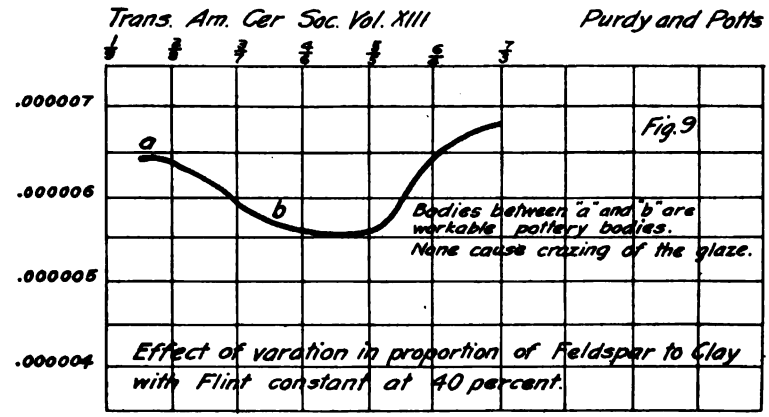
From the curves it will be seen that the maximum expansion occurs when any one of the components of the mixture is high but that the amount of each required to



produce an equally large coefficient differs. For instance, a coefficient of expansion of about 0.0,000,065 was obtained in bodies containing 55 of flint, 45 of feldspar and 50 of



clay respectively, and, furthermore, the expansion of all the 35 per cent. feldspar bodies is nearly the same as is the case in those containing 55 per cent. of flint, while

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to have high expansion due to high clay the feldspar must be low. These observations lead to the obvious conclusion that in amounts above 30 per cent., feldspar is more of a factor in causing an increase in the coefficient of expansion than is flint or clay. In fact, the body with 50 per cent. feldspar has the same coefficients as the one containing 70 per cent. flint, the clay content in each being the same.

(9) From Plate 11, it is to be seen that to obtain a minimum coefficient of expansion requires a progressively decreasing ratio of flint to feldspar with each increase in content of clay. As the clay increases from 25 to 60 per cent., the feldspar content of the minimum coefficient bodies varies from 30 to 25 per cent., producing the valley which, in Fig. 4, is seen to run nearly parallel to the feldspar base.

CONCLUSIONS.

(1) It appears that the coefficient of expansion of white ware body mixtures is more a function of the structure attained than of their mineral constitution.

(*a*) As the feldspar increases above 30 per cent., the development of bleb structure increases quite rapidly. In this series, the body containing 50 per cent. feldspar had developed a bleb structure at cone 10 sufficient to cause it to be swollen.

(*b*) As the feldspar decreases from 25 to 10 per cent., the volume of open pores at cone 10 increases.

(*c*) The bodies containing high flint or high clay will be more porous than the one in which the two mineral substances are in nearly equal proportions.

(*d*) Electrical porcelain bodies of the highest dielectric strength contain from 25 to 35 per cent. feldspar, and it has been repeatedly proven by Mr. Watts that the dielectric strength of porcelain increases with increase in density of structure.

(*e*) We are unable to even conjecture what the influence of degree of vitrification will be on a given body

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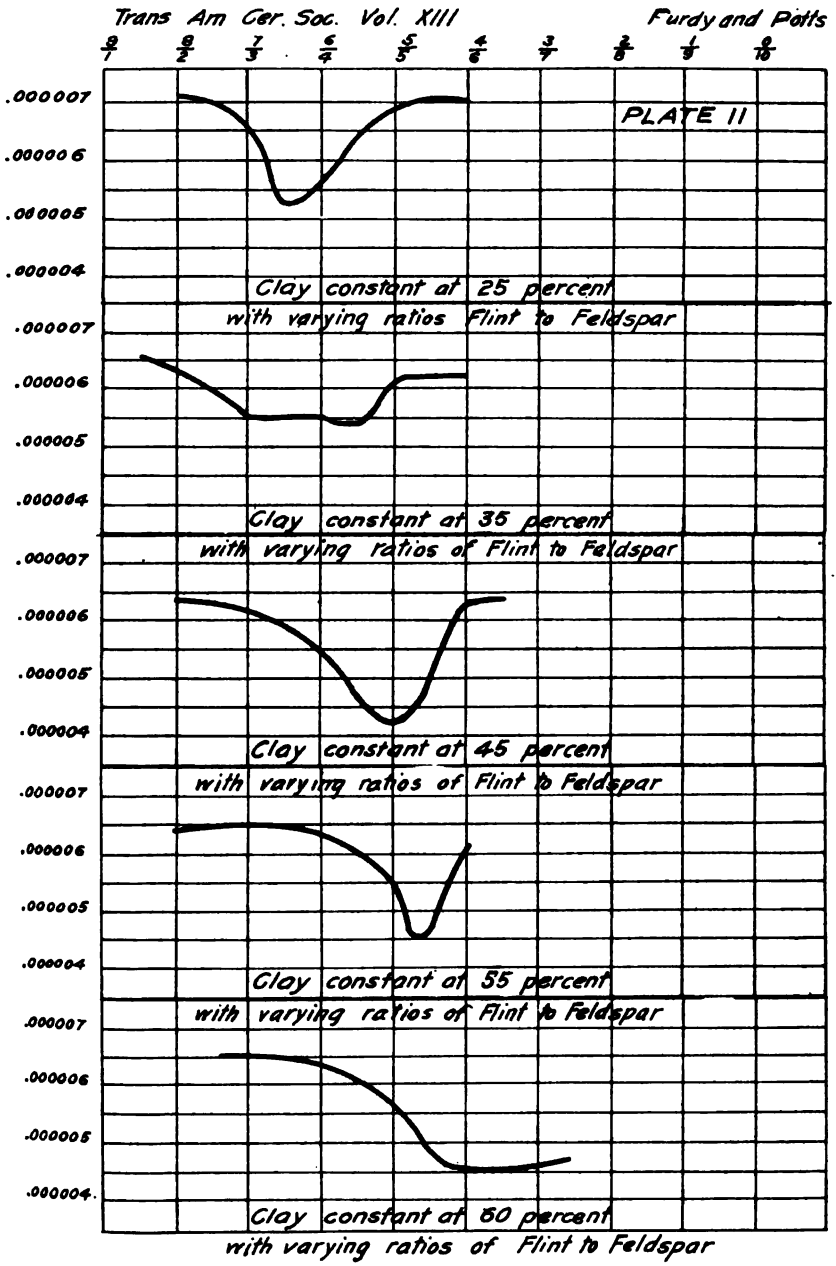

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mixture, but if this supposition proves to be true, we will find in the work now in progress that with increasing heat treatment, the line of minimum coefficient of expansion will progress from high feldspar to lower feldspar content.

(2) While we feel unwarranted in saying that difference in coefficient of expansion of the body and the glaze is wholly without effect on glaze fit, we certainly are forced to recognize that the difference in expansion is neither the sole nor the most effective cause.

Even Seger's rules, as he states them, are contradictory in logic. He says that if the glaze has a greater contraction than the body, the glaze, on cooling, would crack. That much of his argument is quite plausible. But if the glaze has the larger coefficient of contraction, it must also have the larger coefficient of expansion, and, hence, to be logical in his conceptions of the situation, he should have conceded that the glaze would shiver when the ware was heated. But since no one has yet found crazing and shivering under one and the same set of conditions, we must conclude that Seger's ideas concerning the cause of crazing is neither logical in conception nor in harmony with facts.

(3) Since in other studies, we have found, as did Hecht, that a white ware glaze stood equally well on bodies ranging from those high in feldspar, which develop a vesicular structure when vitrified, to those high in flint which, with the same biscuit heat treatment, are not vitrified, *i. e.*, still have open pores, it might be argued that porosity, whether sealed or open, facilitates perfect adjustment between the glaze and body. And, since our observations concerning coefficient of expansion lead us to conclude that it was more a function of the density of structure than of composition and since we find the higher feldspar-flint bodies have more uniformly high coefficient of expansion, we would have both perfect glaze fit and high coefficient of expansion function of the same factor, *i. e.*, density of structure, but not necessarily of one another.

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Not having data on the comparative structural density of our trial bodies, we do not feel warranted in conjecturing in just what way these three factors may be interrelated.

(4) If our findings are confirmed by those obtained on bodies made from other materials, we can say that to produce bodies of low coefficient of expansion and contraction at cone 10, the feldspar content should be between 25 and 30 per cent. of the total mixture, and that the clay should not be lower than 40 per cent. And if our deduction concerning the cause of differences in coefficient of expansion proves to be true, it would be found advantageous in the making of low coefficient ware to employ every device, mechanical or otherwise, that would increase the structural density.

Lag in the Trial Pieces.—No lag in contraction, or permanent set, as it has been called, could be detected, although every night the last piece tested was left in the furnace and remeasured after 15 hours' cooling. We never failed to find that the test pieces had returned to exactly the same length as before heating.

T. G. Bedford writes of his experience: "There seems to have been permanent changes in the length of the tube during the course of the experiments, but these changes are very small and apparently irregular. . . . . The total increase in length at 0° from March 13th to April 18th was 0.02 per cent."

DISCUSSION.

Mr. Binns: I am interested in the model. It elucidates in such a novel manner the fact that the excess of any one component produces the same coefficient of expansion as the excess of another.

We want data of this kind to show the actual behavior of the body mixture, apart from the glaze.

In dealing with any body under a given glaze, you cannot ignore the fact that the glaze is feeding on the body-substance, dissolving certain parts of the body and incorporating them into its own nature. A body

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high in flint is more apt to do so than is one high in clay or in feldspar. That, I think, accounts for the fact that we do not find the same behavior in glazes on bodies as would be indicated by this splendid diagram.

You are aware that a large amount of German product is imported because of its low coefficient of expansion, and that our potters have been only comparatively successful in competing with these imported articles. All kinds of hypotheses have been put forth as to the ingredients used. We have analyzed them and found nothing there but normal ingredients. By means of this diagram, I think that we can, however, approach pretty near to a satisfactory solution of the problem.

Mr. Purdy: We have made little porcelain crucibles out of these same bodies (burned at cone 10), which, when placed in a Caulkins kiln and heated to redness, and then ducked in water, failed to show any relation between the coefficient of expansion and contraction and ability to stand that test.

Mr. Parmelee: Crazing is known to be a very complicated thing, and the fact that we get this scirrhous surface may be explained on the ground that elasticity is a much greater factor than it has hitherto been considered to be in crazing of a glaze.

SUBMITTED AFTER HAVING READ THE PAPER.

Mr. Watts: It is interesting to note that while many areas exist within which a slight change in composition might cause a great change in coefficient of expansion, these areas all lie outside the limits of practical white ware bodies.

A comparison of the findings of these investigators working with American materials at cone 10 and my own findings when using European materials and firing at cone 15 is very interesting as throwing some light on the possible difference in opinions existing as to the rôle of the various constituents in the matured body.

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These investigators find that, within white ware limits, an increase in feldspar at the expense of flint, with clay remaining constant, causes a decrease in coefficient of expansion. This checks my findings at cone 15 on bodies of these compositions.

Within the above limits these investigators find that an increase of feldspar at the expense of clay, with flint remaining constant, decreases the coefficient of expansion, but does not affect the glaze fit as it would be expected to do from Seger's laws.

My findings at cone 15 indicate that very little change in coefficient of expansion would result from the above change in composition.

This difference in action of clay at cone 10 and at cone 15 on given mixtures of flint and feldspar can be accounted for by the fact that at cone 10 the formation of sillimanite by decomposition of clay substance has occurred in very slight degree, while at cone 15 it has progressed much farther and often, according to Zoellner, amounting to a change of 25 per cent. of the clay substance present. If this is the cause of the difference in coefficient at the two temperatures, the sillimanite must possess a very low coefficient of expansion, since it counteracts the influence of the remaining clay substance toward increasing the coefficient of expansion as it does at cone 10 when replacing feldspar.

These investigators find that within the practical limits of white ware body compositions at cone 10 with feldspar constant, an increase of clay at the expense of flint gives a slight increase in the coefficient of expansion.

I found at cone 15 that under such conditions and within these limits a very pronounced decrease in coefficient was obtained.

Why flint should be more active at cone 15 than at cone 10, I cannot explain. We know, however, that a glass containing a given amount of flint possesses a much higher coefficient of expansion than a porcelain containing the same amount of flint.

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A comparative study of bodies fired at cone 10 and cone 15 indicates that at cone 10 the minimum coefficient of expansion is found in bodies containing about 30 per cent. feldspar while at cone 15 the bodies with minimum coefficient of expansion contain about 15 per cent. feldspar. Along either of the above lines the coefficient of expansion increases with increase of flint, although in the cone 10 study this increase is not a uniform rise but, nevertheless, a general one from one extreme of the study to the other. It must be borne in mind that this 30 per cent. feldspar content at cone 10 lies outside the white ware area and, hence, is not used in comparison of bodies in that class. I merely cite the general fact that in bodies of the minimum coefficient of expansion at the two named temperatures, the laws of Seger hold good, *i. e.*, that flint replacing clay increases the coefficient of expansion.

NOTE WRITTEN AFTER READING DISCUSSION BY MR. WATTS.

Mr. Potts: In order to make clearer the relation of Mr. Watts' series to our own and to compare the results obtained under widely different conditions, I have prepared the curves shown in Plate. I. Mr. Watts' curves are shown in full black lines and the points determined by him are represented by solid black dots, while our results are shown by dotted lines and our points by small circles.

The Effect of Variation in Ratio of Feldspar to Flint with Clay Constant.—Within the area investigated by Mr. Watts, three points are evident.

(1) The general trend of the curves is the same.

(2) Mr. Watts' curve has reached its minimum with feldspar and flint in the ratio of 4/6, while our curve continues to fall with increase of feldspar until the ratio of feldspar to flint is 5/5.

(3) While in the mixtures he studied, he obtained lower coefficients than did we, his minimum coefficient is not lower than that which we found.

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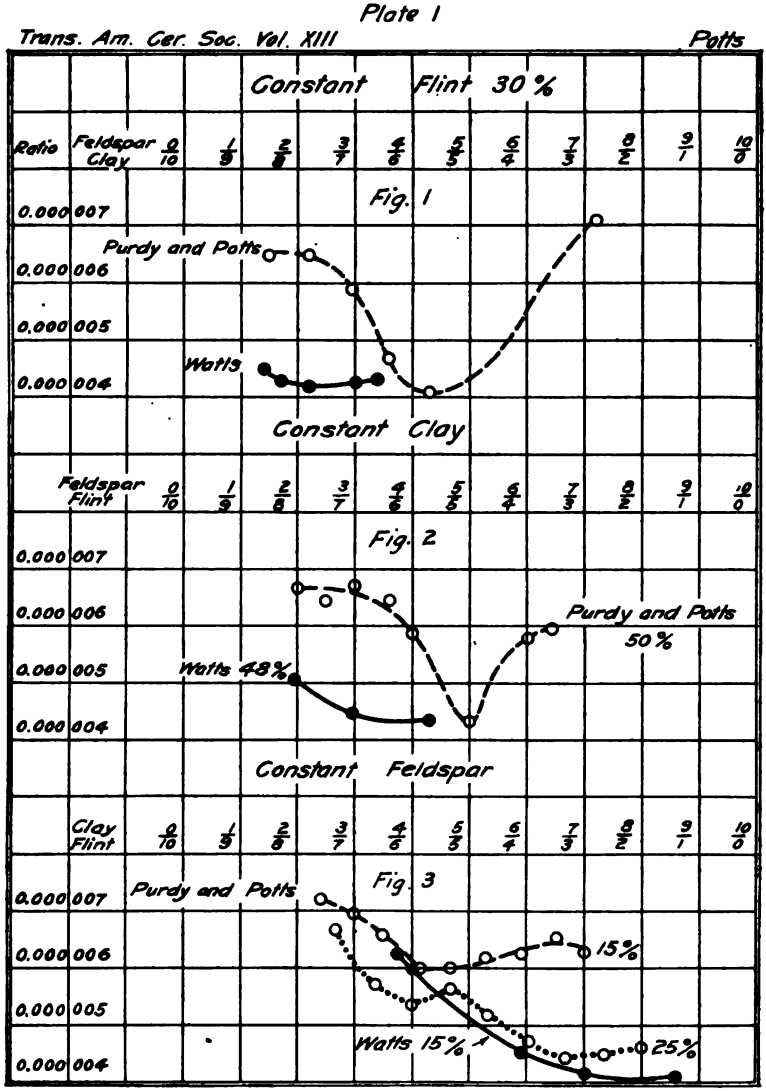
Plate I



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It is well known that at cone 15 the same degree of vitrification and the same development of vesicular structure is obtained with considerably less feldspar than at cone 10. This being the case, these curves show plainly that Mr. Watts' work checks our findings not only as to the fact that within the area of white ware bodies, feldspar decreases the coefficient of expansion but also that the coefficient of expansion is a function of the density of the structure.

At the same time it will be seen that the data of these two papers do not support Mr. Stanley Burt's statement "That up to fairly complete vitrification, the higher we fire, the greater the coefficient" (*Trans. A. C. S.*, Vol. V, p. 342), or the somewhat changed form of the same statement as it appears in Vol. VII, p. 125 of the same *Transactions*. In fact, we find, as did Watts, that the coefficient of expansion decreases as we approach vitrification.

The Effect of Variation in Ratio of Feldspar to Clay with Flint Constant.—The curves showing the effect of these variations tell the same story, *i. e.*, the mixture having the lowest coefficient at cone 15 contains less feldspar than does the one with lowest coefficient at cone 10.

It is very unfortunate that Mr. Watts' series are so short, because, although the evidence is strong that his work supports our findings, it would be much more satisfactory, especially in this matter of the relation of the coefficient of expansion to density of structure, if his curves extended far enough beyond the minimum point to show beyond dispute that an increase of either feldspar or clay would cause an increase in the coefficient of expansion.

It is indeed going quite far into the realm of pure speculation when Mr. Watts attempts to account for the difference in the action of clay under different heat treatments by the formation of sillimanite.

This is amply shown by comparing the curve for constant flint with that for constant clay and noting that there is the same sort of variation in coefficient when the clay is

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constant as when the clay is varying. It will take stronger proof than is now at hand to convince me that the formation of sillimanite *per se* is a factor in reducing the coefficient of expansion.

The Effect of Variation in Ratio of Flint to Clay with Feldspar Constant.—Mr. Watts is surely in error when he says: "We know, however, that a glass containing a given amount of flint possesses a much higher coefficient of expansion than a porcelain containing the same amount of flint." This notion of Mr. Watts' is contrary to the function Seger assigns to the flint used in the body and in the glaze.

I wonder, too, if Mr Watts forgets that silica glass, which Mr. Stanley Burt describes as "fused pure silica" (Vol. V, p. 341, *Trans. A. C. S.*) and which Mr. Watts himself used in the construction of his apparatus, has an extremely low coefficient of expansion.

As for the apparent contradiction in the result obtained in our separate investigations, a study of the two sets of data will show that the contradiction is apparent rather than real.

It will be seen that at the high flint end of Mr. Watts' constant feldspar curve, we each obtained exactly the same values for the coefficient in spite of the difference in the heat treatment which the test pieces received.

It is equally evident that our curve showing ratios of clay to flint of less than 4/6 is merely a continuation of his curve.

The curves do diverge as the clay increases, but, in view of what has been said regarding the relation between density and coefficient of expansion, it is evident why this divergence should be as it is. It is doubtless due to the greater density caused by the more intense heat treatment.

As further evidence of this, the curve showing the coefficient of the bodies containing 25 per cent. of feldspar has been drawn. A glance will show that with clay to flint in ratios greater than 1 : 1, this curve agrees remark-

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ably well with that obtained by Mr. Watts with less feldspar, and a higher heat treatment.

From the very close agreement between Mr. Watts' and our results, it is very evident that there is little ground for difference in opinion as to the rôle played by the various constituents of the matured body. If by matured body is meant the body which is so burned as to have attained the greatest possible density, then the indications are that we agree. Mr. Watts has failed to furnish any data on which to discuss the rôle of the various ingredients in any other than thoroughly vitrified bodies.

It is true that at cone 10 the areas in which slight changes in composition cause a comparatively large change in coefficient of expansion do lie outside of the area of practical white ware pottery bodies. But if the curve showing the effect of variation in ratio of clay to flint is consulted, it will be seen that within the areas of practical bodies, which is represented by the high clay end of the curves, a difference in heat treatment from cone 10 to cone 15 has a more marked effect than has an increase in the feldspar content from 15 to 25 per cent.

In our paper and in this discussion, we have purposely refrained from committing ourselves on the supposed relation between glaze fit and the coefficient of expansion. The data at hand, however, do indicate that there is no such close relation as has been previously held, but we do not wish it to be inferred from this that we believe the difference between the coefficient of the body and that of the glaze is wholly without effect in the control of glaze fit.

Prof. Binns: I have enjoyed the presentation of this paper and particularly the novel and graphic form of the solid diagram. As to the facts there is no room for discussion, presuming the data to be accurate. I do not think the method adopted for measurement is the most accurate possible but Mr. Watts worked, presumably, with another method and secured approximately concordant results. I do not recall any statement as to the

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temperature at which the data for the solid diagram were obtained, or perhaps the figures taken were the averages at all the temperatures dealt with. I should prefer to see the work done at a rise of 100 degrees only as it is between 0 degrees and 100 degrees that crazing occurs and I doubt if the behavior of a given body at 400 degrees or 500 degrees has any necessary bearing on the case.

I am glad to see this work as continuing the study of coefficients. There have been some less important attacks upon the problem but before accepting any new theory the question herein propounded must be answered several times in the same way.

Mr. Potts: I am pleased to have Professor Binns discuss this paper in the way he does, as his remarks show plainly that some points cannot be too strongly emphasized. For example, a considerable portion of the paper is devoted to a discussion of the inaccuracies of the data and the weak points in our method of measurement. But in spite of these, we still have confidence in the relative value of the results obtained and Mr. Watts' results only strengthen that confidence. However, we are not yet satisfied, and as is plainly stated in the paper, plans are under way for a much more extensive, and, we hope, more accurate investigation of the whole subject.

As to the temperature range used, it must be borne in mind that at the outset we did not confine ourselves to an investigation of the subject of crazing alone, but sought to obtain some light on such subjects as, "A Change of Coefficient with Rise of Temperature," "Permanent Set, or Lag in Contraction," and the like, all of which seemed to require as wide a temperature range as possible.

In reply to Professor Binns' inferred question as to the source of data for the solid diagram, I will merely point to the tables where it will be plainly evident that it mattered little which set of results were taken: as a matter of fact, however, the data used are averages of all the results.

The most surprising feature of Professor Binns' dis-

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cussion, however, is the manner in which he utterly ignores the conclusions drawn. These conclusions were purposely expressed in very broad and noncommittal terms, because the results obtained surprised even the investigators, but their trend was so persistently evident as to demand expression. Is it possible that, in our desire to express no more than seemed necessary and this only in very general language, we have so concealed the points that Professor Binns has missed them entirely?

Mr. Binns: Mr. Potts says "we are not satisfied" and still he asks my attention to certain "conclusions." I do not admit conclusions any more than Mr. Potts does. I admit important evidence but am not yet ready to bring in a verdict.

By this I do not mean to criticize or to belittle the work done. It is most excellent but the evidence offered is so radical and so subversive of that which most of us have held that I think it should be abundantly and extensively confirmed before a final judgment is passed.

Mr. Bleininger: I have had the opportunity to read carefully the text of this interesting article, through the courtesy of Professor Purdy. In this connection I must confess that I was preparing to criticize the method of determining the coefficient employed by Messrs. Purdy and Potts based on the objection that the temperature in the box could not have been uniform. But while I still think that a resistance pyrometer[1] using a silver-constantan couple would have more truly represented the average temperature and while, perhaps, the method was not entirely free from optical error due to parallax, it is evident that the results are concordant and are exactly what Professor Purdy claims them to be. Both, the work, and the presentation of the results, and of the conclusions, combine to give us a very fine research upon the successful finish of which the authors are to be congratulated. They deserve the thanks of the Society for this careful and logical contribution.

In the face of their figures any theoretical criticism would be out of place, for they represent scientific facts which silence assumptions of any kind.

[1] See "Measurement of High Temp.," by J. K. Clement, Trans. A. C. S., Vol. XI, p. 457 (Ed.).

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THE EFFECT OF TEMPERATURE ON THE DIELECTRIC STRENGTH OF PORCELAIN INSULATORS.[1]

By CHESTER E. HENDERSON and GEORGE O. WEIMER.

INTRODUCTION.

The Problem. Practical men, having observed the failure of insulators when subjected to abnormally high temperatures, and having been unable to account for this phenomenon, have sent inquiries to various universities for an explanation.

The authors have attempted, in the following work, to obtain data bearing on this problem by subjecting suitable test pieces to electrical strain under a series of temperatures, working on the hypothesis that with an increase in the temperature of the insulator we should find a decrease in the dielectric strength.

The Transformer.—The transformer used for this test was a high tension transformer which has a capacity of 50 kilowatts at 250,000 volts and 60 cycles.

The Electric Furnace.—For the lower temperatures, the test was carried out under oil; but as the flash point of the oil was neared it became necessary to resort to some other means for heating the test pieces, and for these high temperatures, an electric furnace was used. Several different designs of furnaces were discussed, but at last it was decided to make it according to the following design: A porcelain muffle 9″ long, 3″ in diameter, and 3/8″ thick, of the same material as the test pieces, was made, treated, and fired just the same as the insulators. Upon the muffle were wound about 60 turns of No. 19 "Nichrome" wire, a special resistance wire. A thick coating of asbestos paste was plastered over the wires to confine the heat.

THE INVESTIGATION.

Composition of Body.—The body used in this investigation had the following composition:

[1] Done as thesis at the Ohio State University under direction of Ross C. Purdy.

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	Per cent.
Tennessee ball clay, No. 7	27
Tennessee ball clay, No. 3	6
Georgia kaolin	16
American-eureka flint	16
American-eureka feldspar	35

Preparation of Body.—Two batches of two hundred pounds each of the above body were weighed, placed in a large ball mill with about two hundred pounds of water and ground for an hour. The slip was then screened through a one hundred-mesh sieve and filter-pressed. The two batches of body were combined into one and pugged in a small laboratory brick machine. The clay was then placed in stoneware jars (10 gallon capacity) covered with canvass sacks, kept damp by occasional sprinkling with water, and allowed to age for about two months.

After aging, and previous to jiggering, small batches were wedged to proper consistency on a plaster slab.

Properties of the Body.—This clay had excellent working properties, and gave a very low percentage loss in drying and burning. It had the following averages of physical measurements:

Drying shrinkage	4.7%
Firing shrinkage	11.0% (cone 9)
Absorption	0.0% (cone 9)

Forming of the Ware.—The test pieces, which were cylinders 5 1/4″ high, and 3″ in diameter, were formed by jiggering. A ball of the wedged clay was thrown forcibly into the mould and the crucible roughly shaped by means of a "jolly," the tool being then employed to give the final form.

Method of Drying.—The filled moulds were placed in a gas-fired oven to dry. As soon as the moulds would deliver, the crucibles were removed and replaced in the oven to finish drying.

Burning the Ware.—The crucibles were set, bottom down on a cushion of white glass sand, in saggars 7″ deep, 11″ wide, and 21″ long. The ware was burned in the

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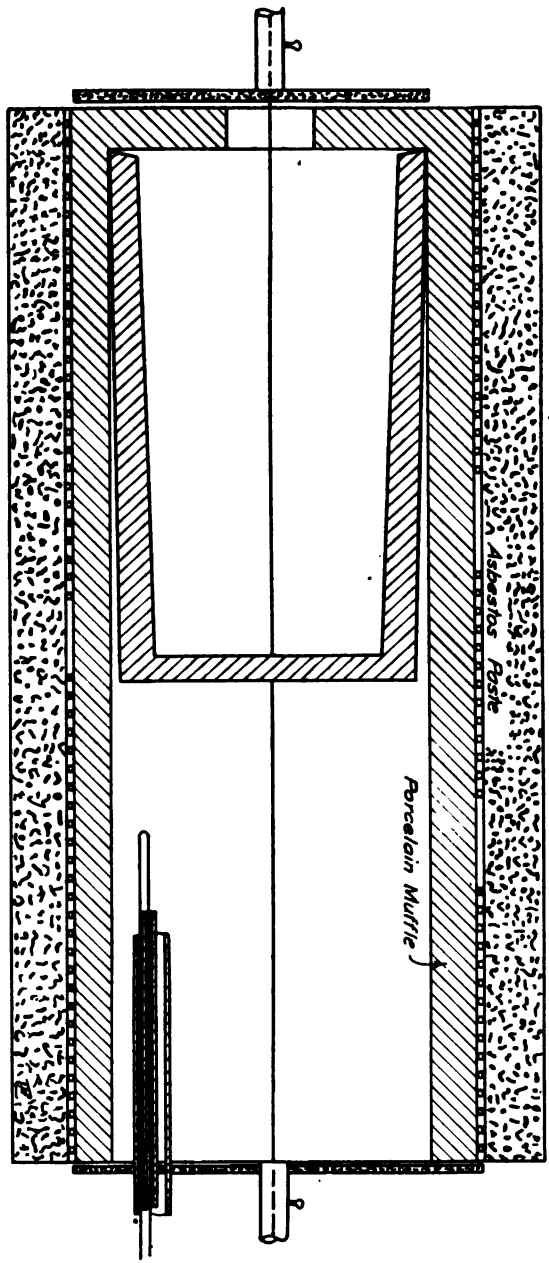

CROSS-SECTION OF ELECTRIC FURNACE
showing test peice in position, thermometer, etc.

Trans. Am. Cer. Soc. Vol. XIII Henderson and Weimer

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No. 1 down-draft kiln, fired with coke. The chamber accommodated four bungs of saggars, three high. These were wadded and securely covered.

The heat treatment was judged by means of Seger

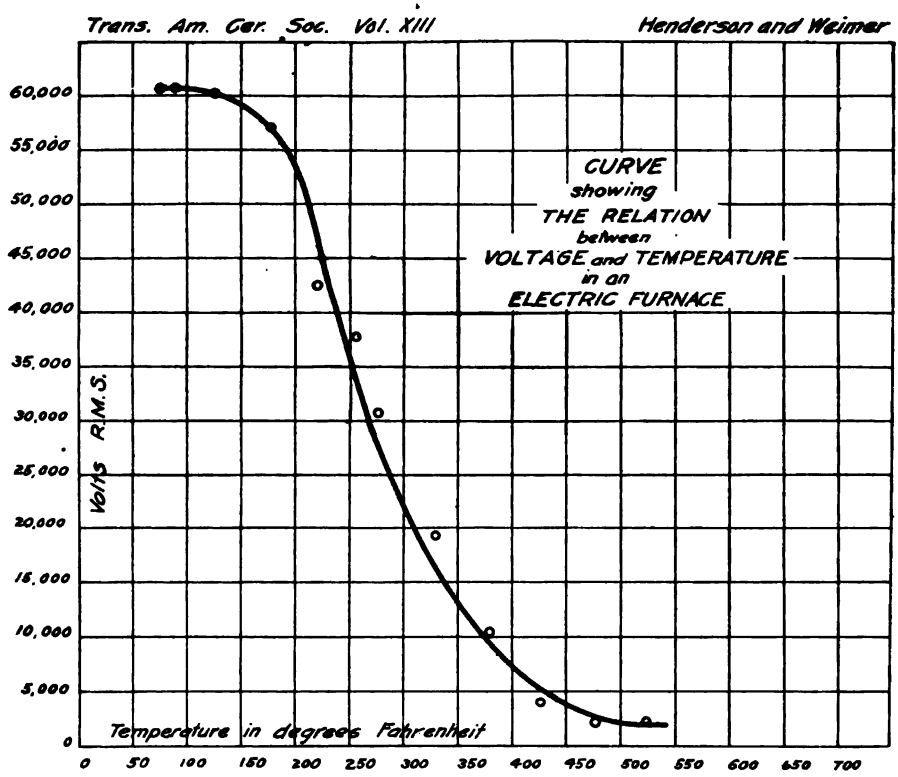

Fig. 1.

cones. Four pats containing cones 9, 10 and 11 were placed in the saggars, one pat in the top and bottom saggar at either end of the chamber. For observation during burning, four pats containing cones 8, 9, 10 and 11 were placed on the covers, one pat on either end of the top saggar of the first and fourth bung.

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Cone 11 was fired down on the outside, and cone 9 in the saggars. Two burns of about 30 hours each were made.

METHODS OF TESTING.

Two methods of testing were used. The first performed under oil, and the second in an electric furnace.

The Method of Testing under Oil.—The test pieces were inserted between the two electrodes, which were made of "Nichrome" wire, and the whole apparatus submerged in oil, as shown in the accompanying photograph. For convenience and safety in heating the oil, it was poured into a large glass beaker, which was partially surrounded by sand contained in a tub. The tub was placed on a sheet-iron plate, resting on a brick support and heated by means of bunsen burners. When the desired temperature (as recorded by means of a thermometer) was reached, the piece was tested. Owing to the low guaranteed flash point of the oil used, it was deemed wise to restrict ourselves to a temperature not greater than 240° F.

Method of Testing in an Electric Furnace.—The accompanying diagram of the electric furnace shows the arrangement of the test pieces and electrodes when puncturing. When temperature tests were made, the insulators were heated in a loose sand bath to approximately the desired temperature before inserting them into a furnace.

Data Obtained as Average on 10 Pieces.

Test No.	Temp. in degrees F.	Puncture voltage	Remarks
1.....	70	47500	Tested in oil.
2.....	190	44000	"
3.....	240	42700	"

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Test No.	Temp. in degrees F.	Puncture voltage	Remarks
1.....	75	60700	Tested in electric furnace.
2.....	125	60100	"
3.....	175	57300	"
4.....	225	42500	"
5.....	275	30250	"
6.....	325	19750	"
7.....	3·5	10500	"
8.....	425	4000	"
9.....	475	2500	"
10.....	525	2000	"

GENERAL REMARKS.

Reasons for not Reducing Voltages to a Standard Thickness.—Ten separate test pieces were calibrated (see data below) and a maximum difference of thickness of 0.020" was found. At the puncturing voltage in air, it was found that one division of the voltmeter scale corresponded to 6000 volts; also figuring that a standard size, 0.21" thick piece requires 60,000 volts, 0.020" would require 6000 volts; hence, from the above it follows that the difference of thickness is within the liability of error in reading the voltmeter.

Number of piece.	Thickness Inch
1.....	0.210
2.....	0.214
3.....	0.219
4.....	0.217
5.....	0.218
6.....	0.226
7.....	0.206
8.....	0.213
9.....	0.299
10.....	0.207
Average thickness.....	0.210

Very few of the insulators were cracked by puncturing. When tested under oil, no arcing occurred; when

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tested in air they arced before puncturing at the lower temperature. At the higher temperatures no arcing occurred and the deflections were quite regular.

After the above data had been obtained, it was suggested that we take some of the insulators, presumably punctured at the higher temperatures, and retest them at room temperature. To our surprise, six pieces at random from those tested at high temperatures showed no indications of ever having been punctured; arcing occurred and a high voltage was required to puncture them. Time and material prevented us from making any further investigations.

The result obtained under oil is not all comparable with that obtained by puncturing with air as a medium.

From the above data it appears that this porcelain changes from an insulator at the lower temperatures to an electrolytic conductor at the higher temperatures.

For future investigation the authors recommend the study of this porcelain at about 400° F., the temperature at which the change probably occurs.[1]

DISCUSSION.

Mr. Binns: How did you protect the thermocouple from short-circuiting?

Mr. Purdy: The thermocouple was removed when attempting to puncture the porcelain.

Mr. Binns: I should like to ask whether Mr. Purdy has formulated any hypothesis as to the influence of the composition of the porcelain on this point.

Mr. Purdy: That question was not taken up at all. We have not attempted to do any theorizing upon it.

Mr. Stover: I have some data on that subject. I have never been able to find the principle, but Dr. C. B. Thwing, professor of physics in the Wisconsin University, had a formula for figuring the electric capacity of materials. I figured out the materials which are used in making our wares, as follows:

[1] See Trans. A. C. S., Vol. IV, p. 97, for similar results on glass quoted by Watts (Ed.).

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Material		Electrical inductive capacity
Water	H_2O	2.6
Boracic acid	B_2O_3	3.8
Silicon	SiO_2 (In the amorphous state and crystalline state.)	6.9
Phosphorus	P_2O_5	6.2
Sodium	Mn_2O	6.6
Potassium	K_2O	6.9
Lime oxide	CaO	8.2
Magnesium oxide	MgO	8.8
Aluminum	Al_2O_3	10.0
Arsenic	As_2O_3	10.6
Barium oxide	BaO	13.0
Zinc oxide	ZnO	14.7
Lead oxide	PbO	24.0
Tin oxide	SnO_2	15.1

2.6 × density = electrical inductive capacity.

Now these are the electrical inductive capacity of these materials as figured on the Thwing formula. The formula was on the basis of 2.6 times the density. I submitted these figures to Dr. Thwing and he said that they were correct.

Mr. Binns: If I recall aright, Mr. Watts, in his paper on electrical porcelain, alluded to the glassy content of the porcelain as influencing its dielectric strength. I think that this is rather important, for it would seem perfectly possible that a porcelain might be composed that would offer more resistance than another. In the ordinary usage of insulator, naturally heated up by the electric current, at what point does it become heated in practice on the passage of a high-tension current?

Mr. Watts: A good insulator in practice is not likely to heat up at all, except in the sun's rays. Of course, there are instances in which they are subjected to the heat of the sun. In that case they become very hot; and this decreases their insulating value as evidenced by the fact

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that in hot climates people have had trouble with the same insulators which work well when cold.

The value of an insulator is in proportion to its resistance to electrical conductivity. If on being heated by the sun's rays the insulators should begin to conduct, it will be further heated by the current passing through it until it either punctures or ceases to be an insulator at all.

Mr. Purdy: The next point for investigation is whether a porcelain insulator is a conductor at all at temperatures below 400° F. If insulators were heated up from room temperature under a stress of about 20,000 volts to the temperature at which it would puncture, would there be any conduction by the insulator prior to being punctured?

Mr. Parmelee: How does this fact enter into the construction of the wired electric furnace with porcelain plate, for instance, such as you showed yesterday with the expansion test? Is there any record of puncture of these plates?

Mr. Purdy: No. In that case it becomes a question of which of the two materials offers the most resistance at the temperature attained.

We have just had a case of another sort but which involves this same phenomenon. The students made a furnace by winding nickel-chrome wire around a porcelain tube, packing the wound tube in a thin layer of magnesia paste and finally in asbestos. On the first trial the furnace worked beautifully, no trouble being experienced in obtaining whatever heat we desired. After having cooled to room temperatures, however, they were unable to re-heat it. On taking the furnace apart we found that the magnesia, asbestos, wires and porcelain had been fused to a glass. The glass, when hot, was a conductor, but when cold, it was a non-conductor.

Mr. Stover: The trials of Dr. Thwing make me think that if that were true in all matters, then a fine-ground material or a well fired material would stand heat better than this.

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Mr. Purdy: His formula does not apply here. The true density of porcelain is 2.6 when green, and still is 2.6 when burned to vitrification. Hence, how can we employ his formula? The increased density that you have in mind when you speak of increased degree of vitrification refers only to the structure and not to the material itself.

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RELATIVE SOLUBILITY OF CLAY AND FLINT IN FELDSPAR.

By Ross C. PURDY, Columbus, Ohio.

This subject has been discussed before by Binns,[1] Mellor[2] and Watts.[3] All of these writers agree that in feldspar, clay is more soluble than flint.

Binns based his conclusion on the observation that when he fused clay and feldspar together he obtained a glass which was transparent, while with flint and feldspar the resultant glass was translucent rather than transparent.

Mellor based his conclusion on microscopic evidence that when a mixture of clay and feldspar is heated, the china clay particles appear to lose their identity before those of flint. In his first report he expresses the belief that ball clay is not so readily attacked as china clay, notwithstanding the fact that when heated alone the ball clay begins to fuse at the same temperature (1100° C.) at which the china clay particles begin to lose their identity in the feldspar magma. In his second report, Mellor says that "Under the ordinary conditions of firing in potter's ovens, feldspar can dissolve approximately 20 per cent. of china clay to form a clear glass solution, while feldspar under the same conditions can dissolve about 15 per cent. of flint."

Watts (page 187, *loc. cit.*) quotes Behrens in the conclusion "that the clay substance, on account of its small grains and amorphous condition, is more dissolved by the molten feldspar than is quartz." . . . . . "By the firing of a porcelain containing quartz most of the quartz particles are externally dissolved and covered with a coating of silicate preventing any further attack."

Watts cites Zoellner (page 189, *loc. cit.*), to the effect that specimens without sillimanite structure exhibit a faint earthy yellow translucency and granular fracture,

[1] Trans. Amer. Cer. Soc., Vol. V, page 290.
[2] Trans. Eng. Cer. Soc., Vol. VI, page 75. Trans. Eng. Cer. Soc., Vol. VII, page 97.
[3] Trans. Amer. Cer. Soc., Vol. X, page 187.

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while those with sillimanite structure display highly uniform bluish white translucency[1] and a smooth fracture. Zoellner is further quoted to the effect that feldspar is able, in the heat of the porcelain kiln, to dissolve 14 per cent. clay substance and 60 to 70 per cent. quartz.

On page 197, *loc. cit.*, Watts, in his summary, uses these words: "As a temperature rises, the feldspar becomes more active, dissolving first the clay substance and later the flint particles until at cone 10 the porcelain begins to show evidence of sillimanite crystallization."

On page 199, *loc. cit.*, Watts says: "In the proportion of 70 per cent. clay and 30 per cent. feldspar, and fired at cone 12 in a 40-hour burn, I find that the ball clays display notably less solubility in the fused feldspar than do the china clays, although the ball clay porcelain displays by far the finer texture."[2]

Of the above citations, all but one, that by Zoellner, state that in feldspar, clay is relatively more soluble than flint. Zoellner is the only one of these observers who speaks in quantitative terms; the others merely base their statements on inferences. If Zoellner's explanation of the cause of difference between the transparent and the translucent fusions is correct (and it seems logical), then the basis on which Binns drew his inferences is not tenable. I hesitate in placing confidence in microscopic observations by those who are not thoroughly experienced in this method of study. It requires long experience and careful training to be able to use the microscope with precision. I have attempted this same sort of microscopic study on two different occasions and finally concluded that I was incompetent to report what the microscope could reveal to one trained in microscopic work, and on one of these occasions[3] I referred the matter to an experienced petrographer.

My contribution to this discussion is mainly based

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[1] Compare with Binns, Trans. Amer. Cer. Soc., Vol. V, page 290.
[2] Compare with Mellor, *loc. cit.*
[3] Geol. Surv. of Ill., Bull. 9.

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upon the work which we have done on white ware body mixtures in the laboratory of the Ohio State University.

(1) In the first place, neither we nor any other observer found a eutectic mixture between clay and feldspar, while we, like many others, have found a decided eutectic between feldspar and flint. In the clay-feldspar mixtures, we find none that will deform easier or earlier than will feldspar alone and none which, when completely fused, will be as liquid. With the flint-feldspar mixtures, on the other hand, we find one which will not only deform more easily and much earlier than will feldspar alone, but when fused, is more fluid.

(2) A study of the comparative translucency of 109 mixtures of clay, flint and feldspar, representing the entire area of a triaxial plotting of these bodies, brought out the fact that translucency decreased with increase of clay and that lines of equi-translucency radiated from the flint apex, swinging more and more toward the feldspar corner of the triangle as the biscuit heat treatment increased in intensity.

(3) We found that in the Crammer warpage test we had the maximum warpage in the eutectic area, the tendency to warp being but little affected by flint additions, while it was decidedly decreased with each increase in clay.

(4) Hecht, Bleininger and Stull, and we found that porosity decrease was more rapid in the high flint bodies than in the high clay bodies.

(5) A study of Simonies curves of equi-refractoriness discloses the fact that in every instance, mixtures of equi-refractoriness can contain more flint than clay.

I take all of these as evidences that in feldspar, flint is more soluble than clay.

DISCUSSION.

Mr. Watts: Bünzli found that he could dissolve in feldspar about seventy per cent. of its weight of flint in a crystalline form, and as high as one hundred per cent.

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of the flint in its amorphous form; and Zoellner, at cone 15, found that he could dissolve flint in feldspar to the extent of about sixty per cent. of the volume of the feldspar used.

The proposition, as brought out by microscopic study, rather puzzles me. If you have a body of the composition of, say, thirty per cent. of feldspar, thirty per cent. of flint, and forty per cent. of clay substance, the latter is very finely divided, and forms the bond in the plastic state for the material. If you study the development of the structure of the pieces through the different ranges of firing, you will find that in the above body, up to cone 9, the feldspar exists as spots or isolated particles, enclosed in a scum or thin coating of these small, round globules, like fish-roe, which we are led to assume is clay substance because we cannot account for it in any other way. As the temperature rises, the flint particles remain intact, with sharp edges. As the heat is increased, the particles of clay substance seem to be absorbed into the feldspar. I consider that this must be the case, because, without destroying this barrier of clay substance, which must act as the scum and surround all particles of flint and feldspar, the feldspar could not get to the flint to attack it. Even with increased temperature, when this evidence of clay substance has entirely disappeared, you still have your particles of flint. The conclusion that I draw from this is, therefore, that the feldspar must attack the clay substance before it can get at the flint, and that then it does undoubtedly attack the gray particles of flint. The chief drawback in an investigation of this point would be the difficulty of obtaining the flint in such a fine state of division that you could compare the solubility of the one with that of the other. If you do not do that, you must fuse and re-fuse, until you get the maximum amount of the two substances in solution, as Day and Allen did. I do not think that from the study of microscope slides we can tell anything about the true solubility of one or the other

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of these materials, that is, the relative solubility; because we are misled by the fact that the flint particles are so much larger.

The actual data indicate that flint is more soluble than clay. I am not prepared to contradict that, nor to admit that it is correct. If a given quantity of feldspar is saturated with flint at a given temperature, it probably could not then take into solution the full amount of clay substance which it would be able to dissolve, if no flint were present and *vice versa*.

The feldspar might take clay substance into solution and make a more viscous mixture. At the same time, it might take flint into solution. There is the proposition of the fluidity of the resultant molten mass, as well as the problem of the solubility. Warpage does not depend entirely on solubility, but on the fluidity of the resultant fusion.

Mr. Binns: I should like to ask what evidence there is of solubility at all? Mr. Watts stated that a certain investigator had found that a large amount of one substance was dissolved in another. How does he know that? What is the test of solubility?

Mr. Watts: I cannot tell. The investigator was evidently of sufficient standing to impress those to whom he spoke, for they did not dispute his statement. Bünzli is considered an authority on such things, and Zoellner is a man recognized as a leader in the circles in which he goes, and I took their statements for facts.

Mr. Binns: The remark that I made was based on this fact, *i. e.*, that when I made a mixture of feldspar and clay, I got an almost transparent glass, but that as soon as flint was introduced the mass began to be opaque, and became apparently more and more white and opaque as the flint increased in amount. I therefore deduced the apparently obvious conclusion that clay dissolved in feldspar, and flint did not. The evidence of the eutectic point between feldspar and flint does not necessarily cover this point, because I do not know that there is neces-

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sarily any connection between the mutual solubility of the substance and the point of the eutectic. We do not consider the actual fusing point, or melting point, or whatever it should be called, a eutectic. I will use, as an example, Belleek, which contains a very small proportion of flint. It is more translucent than a body burning at the same fire in which the flint is in excess. The feldspar seems to have taken the clay into solution. On the other hand, when flint is added to a similar body, it at once increases its opacity. I drew these conclusions, but do not want to insist upon the view, except to stimulate discussion and to point out the necessity of being careful to use terms expressing exactly what we mean.

Mr. Eleod: It is known that in making china without ball clay, the deforming point is much closer to the point of vitrification. As soon as you use the ball clay, the distance between the point of vitrification and the deforming point is gradually increased from two to four cones.

Mr. Watts: In connection with what Professor Binns said, I should like to explain that the customary method of determining solubility in some of the research laboratories of Europe is by the use of polarized light. I know that in some investigations of the solubility of other materials, and also in connection with some determinations of the solubility of flint, they made slides and studied them under the microscope; and by means of polarized light, noted whether there was any evidence of another material being there. I was told that this was the best indication that they had, or that was in the possession of the persons with whom I was talking of the existence of a foreign material in the molten mass. I think that the researches on the solubility of flint in feldspar were made by means of this method.

Mr. Binns: I think that this method is adequate in dealing with the solubility of flint. The fused feldspar would be black in the polarized field, and you would see only the crystals of undissolved flint, as they caught the

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light. The clay is not crystalline and it would be seen as well in the open field as with polarized light.

Mr. Bleininger: The difficulty of microscopic examinations with reference to solution has been exaggerated. While, of course, the ceramist cannot be expected to determine by the customary methods (index of refraction) the crystalline systems of the bodies formed, he should be able to determine a case of solution.

Mr. Watts: I am not discussing the problem of determining to what extent clay substance is dissolved in feldspar, but flint.

Mr. Purdy: You use less temperature, less time, and less effort to get flint into solution, and since solubility is merely a relative proposition, flint must be more soluble than clay.

Mr. Bleininger: I should like to ask Mr. Purdy whether he has made these experiments with the temperature constant?

Mr. Purdy: Our only experience with heating these mixtures at a constant temperature is the burning of these 109 trials at one and the same time in a kiln. We found the greatest translucency, greatest liability to warping, least porosity, etc., in the flint-feldspar part of the diagram. We have never attempted to make a careful fusion between feldspar and flint, nor to determine the relative solubility of clay and flint in feldspar. That is a proposition beyond the possibilities of our equipment, but Mr. Watts has quoted the figures showing that flint is much more soluble than clay, and our practical experience checks that.

NOTE PREPARED AFTER HAVING READ THE PAPER.

Mr. Binns: Prof. Purdy criticizes other investigators for indulging in "inferences" but he himself draws larger inferences than any one. Admitting that his statements as to eutectics and deformation are correct there is no evidence whatever that a reference of these phenomena to solution is anything but an inference.

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To illustrate from aqueous solutions the more soluble a substance is, the more viscous will the solution be. A salt like calcium chloride can be brought into a solution which has almost the consistency of a syrup, while a solution of a sparingly soluble salt will be almost as fluid as water. From this it may be argued that the solubility of clay in feldspar is the direct cause of the absence of deformability from which Prof. Purdy draws his inference. Another point may be mentioned in regard to the microscopic examination. In a mixture of feldspar and quartz, as soon as the temperature becomes sufficiently high, *i. e.*, "in the heat of the porcelain kiln," the quartz grains lose their crystalline structure without entering into solution. Their outlines can be clearly perceived after they have ceased to show any extinction phenomena between crossed nicols. I hesitate to question the accuracy of an observer like Zoellner but the fact mentioned must be taken into account.

I think a good deal of the difference of opinion lies in a lack of standardization. In order to be comparable, the experiments should be made with quartz, clay and feldspar of the same nature and the same size of grain. There will be great differences in results when any source of variation is introduced.

Mr. Kerr: The work of various investigators has tended to show that when flint and feldspar are fused together a eutectic is formed, while in clay-feldspar mixtures no evidences of a eutectic have as yet been reported. In several papers, Prof. Purdy has reviewed the work done by these investigators.

In the fusing of any ceramic mixture the fundamental phenomena are (1) the liquefaction of some one part of the mixture and (2) a subsequent dissolving of the remainder of the mixture in the liquefied part. Of course, in complex mixtures, secondary fusion and solution phenomena must complicate the situation, but in all cases the essential phenomena are a fusion of a part and a dis-

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solving of the remainder in the fused part. Now in clay-feldspar mixtures, the phenomena of fusing, so far as we are now able to judge, consists of the liquefaction of the feldspar and then the dissolving of the clay in the liquid feldspar. In the flint-feldspar mixtures on the other hand, the first thing to liquefy is the eutectic and following that, the excess of either flint or feldspar (which ever one is present in greater proportion than that representing the eutectic mixture) is dissolved *in the eutectic*. Strictly speaking, we cannot refer to the solubility of flint in feldspar, because the flint (if present in excess of eutectic proportions) dissolves not in the feldspar but in the eutectic; and if the flint be present in less than eutectic proportions it will go with part of the feldspar to form the eutectic and the remainder of the feldspar will be dissolved in this eutectic. We must not lose sight of the exceedingly vital point—what constitutes the actual solvent in any particular case.

There is one point to which special attention should be called; *i. e.*, the nature of the feldspar used. The same consideration should probably be applied to all materials used but in the present instance the feldspar is apt to be the most misleading. The various investigators have not used pure feldspars of known composition and properties and it is easily conceivable that the variations in results obtained might be traced to differences in the original feldspars. It is quite certain that a pure orthoclase would give results quite different from those obtained with an impure oligoclase containing a relatively high percentage of clayey and siliceous materials. It should be especially urged that for laboratory investigations bearing upon points such as the one under discussion, the materials should be as pure crystalline materials as it is possible to obtain. Especially is this true with feldspars.

Perhaps the fact that Dr. Mellor's results disagree with those of Zoellner, for instance, is due to differences in the feldspars. Certainly, the fact that Dr. Mellor stands as the foremost physical chemist interested in ceramic

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work and as one of the greatest physical chemists of the day, must add great weight to his opinion.

But taking all present data into consideration one must agree, in substance, with Prof. Purdy, that in feldspar-flint as compared with feldspar-clay mixtures, under similar conditions, more flint than clay is taken into solution. In feldspar-flint mixtures the eutectic is the solvent; in feldspar-clay mixtures, the feldspar is the solvent.

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THE CAUSE AND CONTROL OF THE MOTTLING OF ENAMELS ON METAL.

By HOMER F. STALEY, Columbus, Ohio.

In order to be readily salable, one coat gray enameled ware must have a rather evenly mottled or spotted, light gray surface. In evenly coated ware the gray background is the natural color produced by covering the steel with enamel. The darker spots are due to the production of corresponding spots of ferric oxide precipitate in the enamel coat before it is fired.

The production and control of these dark colored mottles is an interesting application of chemistry to manufacturing. While the principles involved are rather simple, the conditions of success fall within quite narrow limits at several points in the process, and narrow limits are hard to observe in a factory.

The steel shapes are first annealed, then pickled in acid to remove oxide and scale. Either H_2SO_4 or HCl may be used as pickling acid. If oil of vitriol, 65° Bé. H_2SO_4, is used, the solution should contain 10 per cent. acid. If commercial hydrochloric acid is used, the solution should contain 33 1/3 per cent. of the acid. Since 65° Bé. H_2SO_4 contains 90.05% actual H_2SO_4 and commercial hydrochloric (or muriatic) acid contain 27 per cent. actual HCl, these proportions give about 9 per cent. actual acid in the pickling solution. New acid gives a bluish gray cast to the ware and works slowly so some old acid should be present.

The reactions taking place in the pickling tank, using H_2SO_4, are:

(1) $Fe + H_2SO_4 = FeSO_4 + H_2$.
(2) $Fe_2O_3 + 2H_2SO_4 + H_2 = 2FeSO_4 + 3H_2O$.

When clean and bright, the shapes are removed from the pickle, allowed to drain roughly and then quickly conveyed to the enameling room and immersed in a tank

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of water. By this means an amount of acid and $FeSO_4$, rather constant in proportion to the area of steel treated, is transferred to the storage tank which is thus maintained at a rather uniform degree of concentration in H_2SO_4 and $FeSO_4$, sometimes without the knowledge or intention of the operators.

If too much time is lost in transferring the ware to the storage tanks, oxidation takes place, resulting in the formation of a coating of Fe_2O_3 and $FeSO_4$ on the surface of the ware. This coating may not be dissolved in the dilute acid of the storage tank. While Fe_2O_3 is produced intentionally, a little later in the process, it is produced, not as a scum on the steel, but as a stain in the enamel.

When a shape is removed from the storage tank, it is wet with a dilute solution of H_2SO_4 and $FeSO_4$. The enamel slip is rather strongly alkaline from the solution and hydrolysis of finely ground enamel. The reaction may be represented schematically as follows:

$$(3)\quad Na_2SiO_3 + 2HOH = 2NaOH + SiO_2.H_2O.$$

On coating the shape with enamel by dipping, the following reactions take place in the enamel coat:

$$(4)\quad H_2SO_4 + 2NaOH + \text{excess of } NaOH = Na_2SO_4 + 2H_2O + \text{excess of } NaOH.$$

$$(5)\quad FeSO_4 + 2NaOH + \text{excess of } NaOH = FeO.H_2O + Na_2SO_4 + \text{excess of } NaOH.$$

In the warm room the hydrated ferric oxide rapidly oxidizes.

$$(6)\quad 4[FeO.H_2O] + 2H_2O + O_2 = 2[Fe_2O_3.3H_2O].$$

The iron precipitate first appears on the freshly dipped ware as minute green specks of hydrated ferrous oxide. These spots rapidly change to the well-known brown color of hydrated ferric oxide and gradually grow larger. The speed of drying determines the size to which the spots grow, the slower the drying, the larger the spots. Other

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things being equal, the speed of drying also determines the number of spots which appear, the slower the drying the larger the number of spots. Therefore, in order to secure uniform mottling, careful regulation of drying conditions is necessary.

On firing the ware, the iron spots first fuse to the deep red-brown color of anhydrous oxide of iron. On further heating, the red color disappears, leaving the glass transparent. The heavier the iron precipitate, that is, the more concentrated the spots are in iron, the longer must the piece be heated. If the iron content of the spots is too high, the ware will be overfired before they lose their color.

The production of the dark spots by the precipitate of iron oxide does not seem to be due so much to a staining action as to a fluxing action. The presence of the iron causes the spots to fuse to a transparent glass, while the rest of the coat is still opaque, due to undissolved clay or other raw material. If the piece is fired long enough, the light portions gradually lose their color and become indistinguishable from the iron spotted portions.

Since the production of a proper mottling is due to the slight fluxing action of a little oxide of iron, it is clear that uniform grinding of the enamel and coating of the ware is necessary. Any small lump of material and any heavily coated streak or spot will show up as a light spot irrespective of whether it was spotted with iron before firing or not. Likewise, any especially thin spots will burn to a dark color. Poor grinding and dipping will always produce poor mottling.

The conditions that may cause poor mottling may be any of the following:

I. The presence of scales of iron oxide on the ware: This may be caused by insufficient pickling, too much delay in transferring the ware to the storage tanks for pickled shapes, or too much delay between taking the ware from the storage tanks and dipping it. These scales result in an evolution of gas, probably imprisoned air, that causes

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pin holes. If the scale breaks loose from the steel, it floats to the surface of the enamel, causing little rough scabs.

II. Too little hydrated ferrous oxide on the ware: Result would be too few spots.

III. Too much ferrous sulfate on the ware: This may be caused by transfer of too much ferrous sulfate from a pickling vat containing a strong solution of this salt or by the transfer of too much acid which produces ferrous sulfate on the ware in transferring and in storage tank. Also, if the storage tank water is too acid and ware is allowed to stand too long between removal from the tank and dipping, a heavy coating of $FeSO_4$ is formed on it. The result is a heavy precipitate of ferrous oxide on the ware, producing many large spots all high in iron. The ware must be overburned to get rid of the red color.

IV. Allowing the storage tank water to become alkaline: Hydrated ferrous oxide would be produced in the vats and not at all on the ware. This would be an unusual happening as the vat water is generally decidedly acid. There would be a possibility of this taking place, however, if enamel is allowed to get into the vats, for instance from the hands of workmen or from washing off pieces that have to be redipped. Acid is not necessary to produce the spots as shown in equation 5, but it is safest to keep the storage tank water slightly acid.

V. Allowing the enamel to become acid: Result is miserable-looking ware without any true mottling and without a gloss. This might result by means of long continued dipping of ware wet with a strongly acid solution into a slightly alkaline batch. The least soluble enamels would be liable to give this result because their solutions are the least alkaline.

VI. Too long or too hard firing: The white background will become transparent and so destroy the mottling.

In addition to these especially enumerated causes are the defects due to poor grinding and dipping, improper regulation of drying, etc., discussed in the earlier part of this paper. Of course, it will be understood that wherever

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I have mentioned sulphuric acid or one of its salts, hydrochloric acid or one of its salts should be substituted if hydrochloric acid is used for pickling.

The rather common practice of trying to control the mottling by keeping the acidity of the water in the storage tanks uniform does not seem to be feasible. We have attempted to show that an equally important factor in the storage tank water is the content of iron in solution. The iron content of this water as well as the acid content should be kept as nearly uniform as possible.

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RESISTANCE OF SHEET STEEL ENAMELS TO SOLUTION BY ACETIC ACIDS OF VARIOUS STRENGTHS.

By ROBERT D. LANDRUM, Canandaigua, N. Y.

Certain enameled wares have been advertised as capable of withstanding 80 per cent. or 90 per cent. acetic acid solutions, and although this was found to be a true statement still it was misleading, for these very wares were unable to resist the action of ordinary vinegar which contained but 5 per cent. acetic acid. This phenomenon is explained by the chemist as being due to the fact that a 5 per cent. solution of acetic acid is very much more dissociated than one of 80 or 90 per cent. and therefore its dissolving action (which is directly proportional to its dissociation) is much the greater.

To show the action of various mixtures of this common cooking acid and water, the two series of tests were made upon enamels typical of some of the cheap wares on the market.

The First Series of experiments was made upon a gray enamel, mottled with dark brown. As the dark enamel was made up from residues, and as the proportions of the two enamels on the dishes is uncertain, the exact molecular formula of the finished enamel coating cannot be given, but the formulas as calculated from the batch mix of the gray enamel and the analysis of the dark enamel frit (before milling) is given below.

THE ENAMELS.

Soft Gray Enamel.[1]

0.667 Na_2O		1.065 SiO_2
0.108 K_2O		
0.083 CaO	0.272 Al_2O_3	0.402 B_2O_3
0.057 MgO		
0.085 ZnO		0.532 F_2

Milled with 7% clay.

[1] So called, as it is translucent instead of opaque and when milled without tin oxide—as was the case above—the dark ground coat shows through giving a gray effect.

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Soft Dark Enamel for Spray.

0.430 Na_2O		1.700 SiO_2
0.083 K_2O		
0.200 CaO		
0.045 MgO	0.114 Al_2O_3	0.430 B_2O_3
0.056 CuO		
0.010 CoO		
0.176 MnO		0.178 F_2

Milled with 7% clay.

THE TEST.

Nineteen miniature wash-basins about 8.5 centimeters in diameter and 2 centimeters in depth were slushed and burned in a dark colored ground coat, and then dipped into the gray enamel slush and when the excess was shaken off, a light spray of the dark-colored enamel was flipped on with a brush. After drying they were burned at about Seger cone 09 in a muffle furnace. They were cooled in a desiccator and weighed accurately to one-tenth of a milligram (0.0001 gram). Into one of them was accurately measured (from two burettes graduated to 1/10 of a cubic centimeter) 0.25 cubic centimeter acetic acid[1] and 24.75 cubic centimeters distilled water, making a 1 per cent. solution by volume. Into a second dish was measured (as before) sufficient acid and water to make a 2 per cent. solution. Into a third a 3 per cent. and so on as given in the table following. These basins were then placed upon a gas hot-plate and evaporated to dryness without allowing them to boil vigorously.

When baked dry (fifteen minutes after apparent dryness) the dissolved residue was washed out at the tap, the dishes were scrubbed with a finger covered with a rubber finger-stall, rinsed thoroughly with distilled water, placed upon the hot-plate again until dry, cooled in a desiccator and again weighed. The loss in weight, which is equal to the amount of enamel dissolved in each case, is given below in milligrams.

[1] This acetic acid was the ordinary c. p. 99% (1.05 sp. gr.) and by analysis contained 98.99% acid by weight.

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The Results.

Per cent. acid	Enamel dissolved Mg.	Per cent acid	Enamel dissolved Mg.
1	4.8	25	17.9
2	6.9	30	18.9
3	10.1	40	13.0
4	12.1	50	8.9
5	14.9	60	5.0
7	16.9	70	3.1
9	18.5	80	1.6
15	21.3	90	0.3
17	22.0		
20	22.4	100	0.0

The Second Series was undertaken upon an enamel, the definite molecular formula of which can not be given.

The Enamel used was "soft gray enamel," the molecular formula of which is given above.

The Test used was the same as with the first series except that the miniature wash-basins were slushed and burned in three coats, *viz.*, a dark ground, a good opaque white, and the "soft gray enamel" given above which was the top coat. These dishes are on exhibition and the results are given in the following table.

The Results.

Per cent. acetic acid	Enamel dissolved Mg.	Per cent. acetic acid	Enamel dissolved Mg.
1	3.4	21	14.0
2	5.7	23	12.0
3	7.0	25	9.9
4	9.3	30	11.3
5	11.5	40	10.3
7	15.1	50	7.9
9	15.9	60	4.6
11	16.3	70	2.8
13	16.6	80	1.4
15	16.7	90	0.2
17	16.3		
19	14.7	100	0.0

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THE ENAMEL SOLUBILITY CURVES.

The accompanying sketch shows graphically the results of these two series of experiments. The various percentages of acetic acid solutions are laid off horizontally and the lengths of the vertical lines are proportional to the amount of enamel dissolved by the corresponding acid, one centimeter length of vertical line being equal to one milligram of dissolved enamel. The results of the first series, *i. e.*, the one using the mottled enamel, are marked "X", while those of the second series, *i. e.*, of the solid-colored enamel, are marked "⊙".

N. B. The dip of the two curves from 21 per cent. to 30 per cent. acid is unexplained. Several independent trials at those points tended towards proving that this dip is not due to experimental error.

DISCUSSION.

Mr. Staley: This paper is interesting and instructive. As a practical method of testing the relative solubility of enamels in acid solutions, the method described has the commendable feature of being easily and rapidly performed. In point of accuracy, it is capable of being materially improved.

The shape of the solubility curve derived is very interesting. That the solubility should decrease as the acid becomes very concentrated is in accord with common experience.[1] But why should the solubility be greatest at 15 to 20 per cent. acid? Dissociation can hardly be at a maximum at this high concentration. Nor are we willing to grant that the solvent action of acetic acid is directly proportional to its dissociation. If we leave out of consideration the possibility that the acid solution may act toward the enamel simply as a solvent, dissolving it as water dissolves sugar, and treat the phenomena as a case of chemical attack by an acid, we must keep in mind the following considerations:

[1] Foerster, "Action of Acids on Glass," Zeitschrf. Instraum., XIII. 457.

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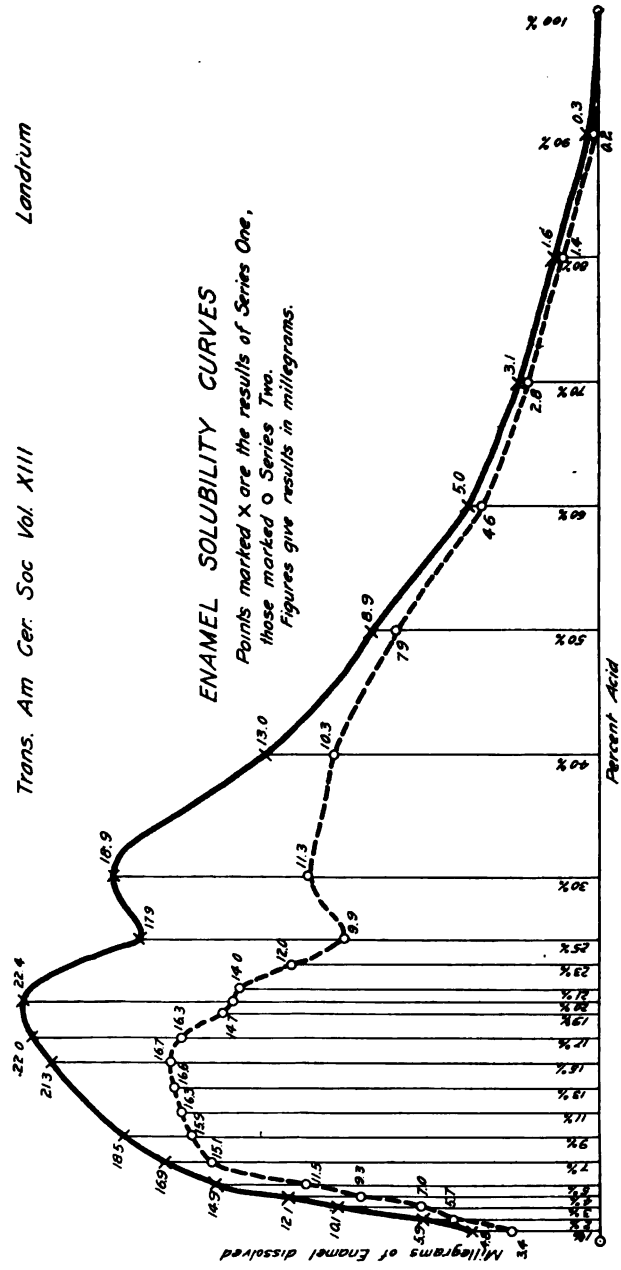

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1. In dilute acid solutions, the acid is more dissociated than in concentrated solutions. This of itself means simply that we will have *more action in a given time per unit of acid* and does not mean that the more highly ionized acid is capable of dissolving more enamel if the reactions are allowed to come to equilibrium.

2. Dilute acid solutions *contain fewer units of acid.*

3. Very highly concentrated acid solutions have little action.

4. The concentration of the acid solutions varied continuously as they were boiled, becoming more and more concentrated as the boiling progressed. Therefore, the more dilute the acid the longer the time in which active concentrations would be operating. It also follows from this that the slower the rate at which the acid is concentrated, the greater will be its solvent action.

In accordance with these conflicting tendencies, we find the acid solutions of maximum solvent action are those of medium concentrations.

Acetic acid is one of the few organic acids that does not form a mixture of constant boiling point with water. The pure acid boils at 118° C. and in water solutions the water will start to come off at 100° C., and will come off the more rapidly the higher the temperature. So, if we should start with a given volume of what would be in this method approximately a 5 per cent. solution by volume of acetic acid and place it on a hot gas plate, we would soon have a smaller volume of 10 per cent., then 20 per cent. and so on up to a very small volume of 100 per cent. acid. The resulting solvent action would probably vary materially from what would be obtained by a treatment for a given time with an acetic acid solution of 5 per cent. strength. The latter results which would truly correspond to the title of the paper under discussion could be obtained by the use of a return condenser.

In order to determine the effect of the rate of evaporation on the solvent action of an acid solution of given

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strength, the following tests were made by the writer. Four pans coated with the same enamel were treated according to this method, the only variation in their treatment being that two pans were placed on a hot portion and two on a cooler portion of the same gas hot-plate. Violent boiling did not occur in either case.

The results are tabulated below:

No. of sample	Per cent. of acetic acid	Time for evaporation in minutes	Enamel dissolved Mg.
1	15	65	20.9
2	15	65	19.1
3	15	155	37.8
4	15	155	39.0

It would seem that in a test of this kind a constant temperature bath should be employed.

Mr. Landrum: I agree with Mr. Staley that my title is rather misleading and might infer that this paper is intended as a research in pure chemistry instead of being merely a statement of the results of a series of practical tests made to demonstrate in a quick and convincing way the fact that an enameled ware may withstand the action of boiling 90 per cent. acid and still be attacked by acid solutions even as dilute as those used in cooking.

In these tests the conditions were very carefully kept as uniform as possible, and I might add that acetic acid and the method of boiling to dryness were used simply because I was trying to duplicate the method used on the ware advertised as "90 per cent. acid proof." I also would like to state that in these series of tests all the dishes in each series were put on the hot plate at the same time and that this plate was of the type giving an even temperature to all parts of the plate (see E. H. Sargent's catalog for cut of plate No. 2406). While, as stated, the solutions were not allowed to boil vigorously, they *were* allowed to boil down as rapidly as possible without spattering. From

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eighteen to twenty minutes were required to boil to dryness.

I certainly do not advocate this as a method for testing the acid-resistance of enameled wares and agree with Mr. Staley that for a research as that seemingly indicated by my title, a constant-temperature bath and a reflux condenser should be used. However, for purposes of duplicating the treatment received by an enameled dish in actual use this method of showing the action of various acetic acid solutions might have some points in its favor over the more accurate one suggested.

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THE CONTROL OF FUSIBILITY IN ENAMELS.

By HOMER F. STALEY, Columbus, O.

Owing to the fact that the use of the conventional empirical formula does not give sufficiently accurate results in iron enamel, I was forced, while making enamels in large quantities, to devise another system of calculation. It is not enough for the successful mixer of cast iron enamels to know what will be the effect in a *general* way of an alteration in his composition—he must know exactly what will be the effect of an alteration of each per cent. Above all, since his firing temperature remains the same and his raw chemicals are expensive, and constantly fluctuating in price, he must know just how many pounds of one material he can substitute for another and get the same physical properties in his enamel and have it mature at the same temperature. The empirical formula does not give this kind of exact information, while the system I wish to describe does. I feel that it gives very accurate control of the physical properties of cast iron enamels.

This system is an example of "Calculation from Empirical Physical Factors." Various series of factors must be determined to control all the physical properties as opacity, solubility, finish, etc. I will describe only the use of factors to control fusibility. As occasion arose over a period of two years, I would cut out of the mix I was using, in a commercial way, a considerable amount of one material and put in successively increased amounts of some other until I had an enamel of the same fusibility as the one with which I started. The relative fusibility of enamels can be determined very accurately by any experienced person by the way it works when being applied to the ware.

I worked with melted weight of the minerals used because only in this way can the error, due to large and varying amounts of volatile matter, be obviated. I treated each chemical as a unit rather than a mixture of various oxides,

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for only thus could differences of physical condition and chemical combination of the various elements enter into the system of calculation. The melted weights used are calculated from the raw state by the use of factors based upon the conventional assumptions as to volatility of H_2O, CO_2, N_2O_5, etc. No fluorine is supposed to be lost. The actual melted weight will fall from 3 to 5 per cent. below this calculated melted weight, according to the care in charging and emptying the fritt kiln, etc. This extra loss is probably nearly all due to mechanical loss of dust up the flue, and in handling.

In this paper I wish to show how the composition of an enamel may be changed without change in fluidity. As the relative cost of various compositions is a vital matter to enameled ware manufacturers, I will also indicate the cost per pound of each. A saving of one cent a pound on the enamel used will pay 6 per cent. interest on the investment in the entire enameling plant.

In calculating the cost of the enamels, the following prices per pound of the various materials, raw, will be used:

Feldspar.....	$0.0035	Boric acid.....	$0.045	Whiting..	$0.006
Flint.....	0.0040	Soda ash.....	0.0085	ZnO.....	0.055
Fluorspar.....	0.0045	Sodium nitrate...	0.0325	Red lead .	0.0625
Cryolite.....	0.0625	Pearl ash.....	0.075	Bone ash.	0.03
Barium fluoride.	0.0375	Potassium nitrate	0.0525	MnO_2.....	0.0425
Borax.....	0.0340	Barium carbonate.	0.0185	Tin oxide.	0.35

Starting with enamel I (see table p. 511), we wish to make various changes in its composition, but still maintaining its fusibility at the same point, that is, we wish, it to mature at the same temperature. This recipe is the basis of those used in several American plants at the present time. It gives a calculated melted weight of 990 pounds, and a cost of $60.27 or $0.0610 per pound.

The feldspar called for by the numbers given in this recipe is a rather infusible one of the following analysis, and empirical formula:

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SiO_2	70.60			
Al_2O_3	18.12	0.655 K_2O	1.34 Al_2O_3 + Fe_2O_3	8.75 SiO_2
CaO	0.55	0.26 Na_2O		
MgO	0.06	0.085 CaO		
Na_2O	2.15			
K_2O	8.29			

If any other feldspar is used, it must be used in a different ratio. This ratio can be determined by experiment only. The flint used is dry ground potter's flint, such as is furnished by all American potters' supply houses.

Inasmuch as potash salts are more expensive than the corresponding soda salts, we replace pound for pound all K_2O, brought in by soluble salts, by Na_2O from the corresponding soda salts. This gives us Enamel II, melted weight 990, cost $56.95 or $0.0575 per pound.

Since our fusibility remains the same, we have illustrated the following fact:

(*a*) *When introduced from corresponding soluble salts, Na_2O and K_2O are equivalent, pound for pound.*

Na_2O introduced from $NaNO_2$ is more expensive than when introduced from Na_2CO_3. With a properly built melting tank and proper oxidizing condition of kiln gases while fritting, sodium nitrate may be reduced to an amount corresponding to 10 Na_2O to a thousand pounds melted. In fact with care, enamels can be made without the use of any nitrate, but it is safer to have a small amount present. Having carefully regulated our firing conditions, we reduce Na_2O from $NaNO_2$ and replace it, pound for pound, by Na_2O from Na_2CO_3. There is no change in fusibility. We would get the same results, if we replaced K_2O from KnO_3 by K_2O from K_2CO_3. We would get the same results if we introduced our Na_2O from borax, keeping the number of pounds of B_2O_3 the same. This is a demonstration of the fact that:

(*b*) *Na_2O and K_2O, introduced through soluble salts, have the same fluxing power, pound for pound, without reference to the particular soluble salt by which they are introduced.*

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The function of the MnO_2 in our recipes is to counteract the yellow color due to the oxidizing effect of the high amount of $NaNO_3$ used on the iron present as impurity in the batch. Since we have cut down on the amount of $NaNO_3$, we no longer need the MnO_2, and so can drop it from composition. This change, along with the change in relative amount of Na_2O from $NaNO_3$ and Na_2CO_3, gives us Enamel III, melted weight 989, cost $55.55 or $0.0562 per pound melted.

We next replace flint by feldspar. Dropping flint from our batch and adding successive increments of feldspar, we find that *using this particular feldspar*, if we wish to keep the fusibility the same, we must use 1 1/2 pounds of feldspar in place of 1 pound of flint. This is a demonstration of the fact that:

(*c*) *Feldspar can replace flint in an enamel at a ratio to be determined only by experiment with each feldspar.*

This change gives us Enamel IV, melted weight 1014, cost $55.61 or $0.0548 per pound melted. It is to be noted that although our melted weight is increased, we do not increase our tin oxide so the percentage amount of SnO_2 decreases. This is because we find experimentally that replacement of flint by a larger amount of feldspar increases rather than decreases opacity.

Cryolite is an expensive material. All its components, Na, Al and Fl, could be brought in through other minerals, and by proper adjustment, the final composition could be kept the same. Likewise $BaFl_2$ is more expensive than $CaFl_2$. By increasing BaO, from $BaCO_3$, and CaF_2 and decreasing CaO from $CaCO_3$, we would be able to get the same final composition without using BaF_2. If we were to substitute for either Na_3AlF_6 or BaF_2 in that way, we would not get the same fusibility. In other words, the fluorides must be treated as minerals and not mixtures of oxides.

By experiment we find that we may keep fusibility the same by substituting CaF_2 for Na_3AlF_6, pound for pound, and can substitute CaF_2 for BaF_2 in the propor-

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tion of 3 pounds of CaF_2 for 4 pounds of BaF_2. Making these substitutions, we get Enamel V, melted weight 1001.5, cost $52.75 or $0.0528 per pound. We have illustrated the following facts:

(*d*) *The fluorides must be considered as minerals and not as mixtures of oxides.*

(*e*) *Na_3AlF_6 and CaF_2 have the same fluxing power, pound for pound. Three-quarters of a pound of either of these is equal in fluxing power to one pound of BaF_2.*

While bone ash can be used as a weak opacifying agent to some extent, it is liable to cause minute pin holes in the enamel and a vesicular structure in any part of the piece that should happen to be overheated. For these reasons it is desirable to eliminate it from our mix as it can be done without increasing the cost. Bone ash has as strong an influence on raising the fusibility of an enamel as feldspar. When we take out bone ash, we have to put in a little tin in order to keep opacity the same. So if we replace our 36 pounds of bone ash by an equal weight of feldspar, and add 2 pounds of oxide of tin, we will get an enamel of the same fusibility and opacity. This gives us Enamel VI, melted weight 1003.5, cost $52.50 or $0.0523 per pound melted weight. This is a demonstration of the fact that:

(*f*) *Bone ash in small amounts can be replaced by feldspar, pound for pound, without noticeable effect on fusibility.*

A good grade of zinc oxide, corresponding to what is known commercially as "selected" is cheaper than PbO from a good grade of red lead. I have never been able to see any advantage in the use of fancy brands of zinc oxide, such as "Red Seal," Green Seal," etc. We will find by experiment that if we wish to replace 100 pounds of our PbO by ZnO, it will take an equal number of pounds of ZnO.

The enamel high in zinc will be very slightly more opaque than the one high in lead, so we can reduce our tin by 2 pounds. I have made this substitution in these large amounts time and again and was never able to find any one who could pick out the two enamels either from their fusibility, or from the appearance of the ware made

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from them. These changes give us Enamel VII, melted weight 1001.5, cost $50.95 or $0.0510 per pound. This is a demonstration of the fact that:

(g) *ZnO and PbO have the same fluxing power, pound for pound.*

We may wish to still further reduce our lead, and in order to illustrate the ratio between the two substances, suppose we replace PbO by B_2O_3. We will find that it will take 16 pounds of B_2O_3 to replace 20 pounds of PbO. Making this substitution, we get Enamel VIII, melted weight 996.5, cost $50.95 or $0.0510 per pound melted. This substitution can be made in much larger quantities than indicated, but it is not desirable to reduce our lead any lower. This illustrates the fact that:

(h) *One pound of PbO is equal in fluxing power to 0.8 pound of B_2O_3.*

This enamel (VIII) would be too high in B_2O_3 to be economical, so we would reduce B_2O_3 by substituting some other fluxing material for it. If we use BaO from $BaCO_3$, we will find that it will take 20 pounds of BaO to replace 16 pounds of B_2O_3. Since we would be increasing our alkaline earth content, we could cut down on our tin oxide, reducing it 2 pounds. This would give us Enamel IX, weight 999.5, cost $49.45 or $0.0495 per pound melted. This illustrates the fact that:

(i) *One pound of BaO is equal to 0.8 pound of B_2O_3.*

As ZnO is more expensive than BaO it will be an advantage to replace the former by the latter. By experimenting, we will find that if we wish to take out 40 pounds of ZnO and keep fusibility the same, we must put in an equal amount of BaO. As opacity is greater by this change we can reduce SnO_2 by 2 pounds. This will give Enamel X, weight 996.5, cost $47.50 or $0.0477 per pound melted. This illustrates the fact that:

(j) *BaO has the same fluxing power as ZnO, pound for pound.*

If we wish to cut down on BaO and replace it by CaF_2, we will find that it will take 12 pounds of CaF_2 to replace

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20 pounds of BaO. As opacity increases as fluorides increase, we can cut down 2 pounds on our oxide of tin. This gives us Enamel XI, weight 986.5, cost $46.40 or $0.0473 per pound melted weight. This illustrates the fact that:

(*k*) *Six-tenths pound of CaF_2 is equal in fluxing power to 1 pound of BaO.*

Whiting is not used to any large extent in making enamels. CaO from $CaCO_3$ is not an active flux in enamels. The temperature range at which enamels are fritted seems to be too low for calcium carbonate. For this reason only small amounts of it should be used, and these should be kept about constant. For these amounts, it probably has a fluxing power equal, pound for pound, to the other R O. fluxes. The exact relation is hard to determine, since the amount used is so small.

This restriction in the use of calcium does not apply to it as a component of lime-soda feldspars. In this combination, it has a strong fluxing action, as these feldspars are more fusible than pure soda and potash feldspars. Calcium may also be used in large amounts, if introduced in shape of fluorspar. As brought out above, it is ridiculous to group this calcium in an empirical formula with that from $CaCO_3$, and from lime-bearing feldspar. The action of the calcium from the three sources is entirely different.

Now suppose instead of the feldspar we are using, we substitute a soft lime-soda-magnesia feldspar of the following analysis and empirical formula.

Analysis		Formula		
K_2O 1.94				
Na_2O 10.27	0.083 K_2O			
MgO 2.36	0.668 Na_2O	0.813 Al_2O_3	4.35 SiO_2	
CaO 0.14	0.238 MgO			
Al_2O_3 ..... 20.57	0.011 CaO			
SiO_2 ..... 64.62				

We find by experiment that it will take 83 1/3 pounds of this feldspar to replace 50 pounds of flint in an enamel,

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or it will take 83 1/3 pounds of this feldspar to replace 75 pounds of the feldspar we have been using. Substituting the new feldspar for the old in this ratio, we get Enamel XII*a*. Since the total weight of our enamel is greater, we must increase our tin oxide, but since the increase consists of lime-soda feldspar, and not of the fluxes which destroy opacity, we need not increase it in direct proportion to the increase in weight. We add 2 pounds of tin oxide. In order to get Enamel XII*a*, as a basis for comparison with the other enamels, we reduce its melted weight to approximately 1000 pounds. This gives Enamel XII*b*, melted weight 1000, cost $45.54 or $0.0455 per pound. This is an illustration of the fact that:

(*l*) *One feldspar can be substituted for another in an enamel in a ratio to be determined only by experiment.*

This series of recipes is not fitted to illustrate the relation between Na_2O and K_2O, and the metallic oxides, etc., but this has been worked out, and it is found that we can draw the following conclusion:

(*m*) *One pound of Na_2O or K_2O is equal in fluxing power to 1 pound of ZnO, PbO or BaO.*

SUMMARY.

Having checked up these ratios time and again in large batches used in regular factory practice, we are now in a position to generalize.

The following oxides have the same fluxing power, pound for pound:

1. K_2O from soluble salts, Na_2O from soluble salts, BaO from $BaCO_3$, ZnO, PbO.

2. Taking the fluxing power of any one of the above oxides, say PbO as unity, it takes 0.8 pound of either B_2O_3 or BaF_2 to give one unit of fluxing power; that is, these substances have a fluxing power factor of 1 1/4.

3. It takes 0.6 pound of CaF_2 to give one unit of fluxing power; that is, CaF_2 has a fluxing power factor of 1 2/3.

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4. Taking the power of an addition of 1 pound of dry ground flint as our unit of refractoriness, we find that it takes 1 1/2 pounds of the particular feldspar we are using, or of bone ash, to give one unit of refractoriness. In other words, this feldspar and bone ash have a refractoriness factor of 2/3.

5. The full statement of the fusibility of an enamel is embodied in the following formula:[1]

Fluxes (A)		Refraction (B)
K_2O from soluble salts Na_2O from soluble salts BaO from $BaCO_3$ CaO from $CaCO_3$[2] ZnO PbO	x 1 =	Flint x 1 = Feldspar x Y =[2] Bone ash x 2/3 = Sand x Z =[2]
B_2O_3 BaF_2	x 1½ =	
CaF_2 Na_3AlF_6	x 1⅔ =	

If the sum of the fluxing units be represented by A and the sum of the refractory units by B then the fluidity ratio can be represented by A/B.

The empirical fusibility formula of Enamel I is:

57 K_2O 24 Na_2O 15 CaO 10 BaO 50 ZnO 160 PbO	x 1 = 316	50 Flint x 1 311 Feldspar x ⅔ 36 Bone ash x ⅔	= 50 = 207.33 = 24.0 281.
56 B_2O_3 50 BaF_2 65 CaF_2 20 Na_3AlF_6	x 1½ = 132.5 x 1⅔ = 141.66		
	590.		

Fluidity ratio = 590/281 = 2.10 : 1

[1] Y and Z must be determined experimentally for each feldspar and each sand.
[2] For small amounts only.

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The so-called "molecular" formula[1] of Enamel I is:

$$\left.\begin{matrix} 0.209\ K_2O \\ 0.121\ Na_2O \\ 0.001\ MgO \\ 0.269\ CaO \\ 0.083\ BaO \\ 0.147\ ZnO \\ 0.170\ PbO \end{matrix}\right\} \left\{\begin{matrix} 0.132\ Al_2O_3 \end{matrix}\right. \left\{\begin{matrix} 0.07\ SiO_2 \\ 0.27\ Fl_2 \\ 0.19\ B_2O_3 \end{matrix}\right.$$

Oxygen ratio = 1 : 1.94

The empirical fusibility formula of Enamel XII*b* is:

$$\left.\begin{matrix} 78.0\ Na_2O \\ \quad MgO \\ 14.5\ CaO \\ 48.5\ BaO \\ 106.5\ ZnO \\ 38.5\ PbO \end{matrix}\right\} \times 1 = 286 \qquad 456\ \text{Feldspar} \times \tfrac{3}{5} = 273.6$$

$$\left.\begin{matrix} 54.0\ B_2O_3 \\ 130.0\ CaF_2 \end{matrix}\right\} \begin{matrix} \times 1\tfrac{1}{4} = 67.5 \\ \times 1\tfrac{3}{5} = 216.6 \end{matrix}$$

Fluidity ratio = 570/273 = 2.10 : 1

The empirical "molecular" formula[2] of Enamel XII*b* is:

$$\left.\begin{matrix} 0.015\ K_2O \\ 0.286\ Na_2O \\ 0.047\ MgO \\ 0.335\ CaO \\ 0.055\ BaO \\ 0.229\ ZnO \\ 0.030\ PbO \end{matrix}\right\} \left\{\begin{matrix} 0.16\ Al_2O_3 \end{matrix}\right. \left\{\begin{matrix} 0.856\ SiO_2 \\ 0.29\ Fl_2 \\ 0.134\ B_2O_3 \end{matrix}\right.$$

Oxygen ratio = 1 : 1.43.

REMARKS ON THIS METHOD.

This system is strictly empirical, it needs no foundation in theoretical reasoning. The fact that it works is its justification for existence. In proof that it will work, I will state that it has been used during the last five years in several different plants with uniform success.

I can not refrain, however, from making a couple of remarks in reference to it. To ceramists who may express

[1] $CA_3(PO_4)_2$ and SnO_2 are present as opacifying agents and hence not included in the formula.

[2] SnO_2 is present as opacifying agent, hence not put into formula.

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surprise that I should have found the free R O. oxides to have the same fluxing power, pound for pound, I will say that ceramists have been saying substantially this thing for many years. Since the time of Seger[1] we can trace through ceramic literature the idea that the fluxing power in fritted glazes of "equi-molecular" amounts of the various R O. oxides is in proportion to their molecular weights. This is simply another way of saying that pound for pound they have equal fluxing power.

If surprise be expressed that I have grouped together ingredients totally unlike chemically, for instance R O. oxides, B_2O_3 and CaF_2, I reply why should we not? We are attempting to determine the relative effect of these ingredients on the physical properties of our enamel. It is to be taken for granted that substances unlike chemically can have like physical effect, and it is rather ridiculous to classify ingredients chemically when trying to study physical properties.

In closing, let me say that while all the enamels here given have the same fusibility, they do not have all their other properties alike. Opacity, luster, heat range, liability to craze, etc., do not depend entirely upon fusibility, although this has an important bearing on some of the properties mentioned. While the equivalent of every one of these enamels has been used at some time, in some shop, in a commercial way, no one of them is in actual use in the form given at the present time. I could not publish recipes in actual use for obvious reasons. A recipe for an iron enamel is of no value in and of itself. Skill in the manipulations of melting, grinding, application of the enamel to the ware, heating, etc., are of vastly more importance than the possession of a recipe that has given good service at some plant. Probably any one of these recipes would have to be altered to suit special conditions at each plant in which it would be used. These recipes are given not because they represent the best compositions available, or the cheapest, but to illustrate principles by which the enamel, which is the cheapest and best for a plant working under given conditions, can be obtained.

[1] Seger's Collected Writings, page 568.

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Ingredients	Melted weight.												
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII*a*	XIII*b*
Feldspar	311.0	311.0	311	386	386.0	422.0	422.0	422.0	422.0	422.0	422.0	470.0	456.0
SiO_2 from flint	50.0	50.0	50	...	...	...	...	...	...	...	...	...	...
CaF_2	65.0	65.0	65	65	122.5	122.5	122.5	122.5	122.5	122.5	134.5	134.5	130.0
Cryolite, Na_3AlF_6	20.0	20.0	20	20	...	...	...	...	...	...	...	...	...
BaF_2	50.0	50.0	50	50	...	...	...	...	...	...	...	...	...
B_2O_3 from borax	56.0	56.0	56	56	56.0	56.0	56.0	72.0[1]	56.0	56.0	56.0	56.0	54.0
Na_2O from borax	24.0	24.0	24	24	24.0	24.0	24.0	24.0	24.0	24.0	24.0	24.0	23.0
Na_2O from Na_2CO_3	...	29.0	47	47	47.0	47.0	47.0	47.0	47.0	47.0	47.0	47.0	45.5
Na_2O from Na_2O_2	...	28.0	10	10	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	9.5
K_2O from K_2CO_3	29.0	...	...	...	...	...	...	...	...	...	...	...	...
K_2O from KNO_3	28.0	...	...	...	...	...	...	...	...	...	...	...	...
BaO from $BaCO_3$	10.0	10.0	10	10	10.0	10.0	10.0	10.0	30.0	70.0	50.0	50.0	48.5
CaO from $CaCO_3$	15.0	15.0	15	15	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	14.5
ZnO	50.0	50.0	50	50	50.0	50.0	150.0	150.0	150.0	110.0	110.0	110.0	106.5
PbO from Pb_3O_4	160.0	160.0	160	160	160.0	160.0	60.0	40.0	40.0	40.0	40.0	40.0	38.5
Bone ash	36.0	36.0	36	36	36.0	...	...	...	...	...	...	...	...
Tin oxide	85.0	85.0	85	83	85.0	87.0	85.0	85.0	83.0	81.0	79.0	81.0	78.0
MnO_2	1.2	1.2	...	...	...	...	...	...	...	...	...	...	...
Total melted wt.	990.0	990.0	989	1014	1001.5	1003.5	1001.5	996.5	999.5	996.5	986.5	...	1000.0
Cost	$60.27	$56.95	$55.55	$55.61	$52.75	$52.50	$50.75	$50.95	$49.45	47.50	$46.40	...	$45.54
Cost per pound	$.0610	$.0575	$.0562	$.0548	$.0528	$.0523	$.0510	$.0510	$.0495	$.0477	$.0473	...	$.0455

[1] 16 pounds of this B_2O_3 comes from boric acid.

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AN INVESTIGATION ON ART ENAMELING ON METAL.[1]

By JOHANNES MINNEMAN, Barberton, O.

INTRODUCTION.

Definition.—The word enamel in its general usage includes many materials which are not true enamels, such as the hard varnish put upon bicycles and some furniture. As used in ceramics, however, the word enamel includes only silicate compounds, which, when fused into a hard and glassy mass, are opaque.[2] In the jewelry industry, opacity is not a requisite property of the glass. Here the term is justified wholly by usage and not by definition.

Requisite Properties.—An enamel to be used successfully on metal must have the following properties:

(*a*) It must, first of all, adhere so firmly to the metal that it will not scale off with handling.

(*b*) It must not crack or craze with change in temperature.

(*c*) It must be hard enough to stand ordinary wear without losing its brilliancy.

(*d*) It must be insoluble enough to keep this brilliancy when subjected to moisture and slight acidities.

(*e*) The silicate to be used must melt at sufficiently low temperature as not to endanger the metal by oxidation and melting, or to volatilize the metallic oxides used in the enamel for the production of various colors.

Methods of Application.—There are four distinct methods of application, or types of enamels: (*a*) Cloisonné, (*b*) Champlevé, (*c*) Limoges, and (*d*) Pointed Enamels.

(*a*) Cloisonné consists in making small compartments or cloisons on a metal sheet, by soldering fine wire to the surface, filling each compartment with the material of the enamel in a state of powder or paste, and, after drying, firing the plate, thus causing the enamel to fuse and completely fill the cavities.

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[1] Thesis at the Ohio State University under the direction of Ross C. Purdy.

[2] The terms iron "enamels" and wall tile glaze "enamels" are quite common, but according to definition of enamel, are not always correctly used (Ed.).

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(*b*) Champlevé. This resembles Cloisonné, but in this case, the design is executed on a metal plate, and the parts to be filled with enamel are hollowed out to a slight depth, then filled in with enamel and fired as before.

(*c*) The Limoges type is very difficult to execute, and consists of melting transparent enamels upon the surface of metals without the use of any cloisons.

(*d*) Pointed enamels are very similar to pointed porcelain, the difference being that the base is a metal covered with an opaque enamel instead of a porcelain.

Metals Used.—Gold, silver, and copper are all used for enameling; pointed enamels are invariably put upon copper, owing to its cheapness and the fact that opaque enamels are used, so that the metal does not show; but in the other types, silver and gold are often used because these metals, shining through the transparent enamels, produce much more gorgeous colors than copper.

History.—The art of enameling upon metals probably had its origin with the Egyptians when they fastened pieces of colored glass into recesses in the metal of their jewelry. We know that enamel, in its simpler form, was in use among the Egyptians, Phoenicians, Assyrians, Greeks, Romans and Etruscans, but not in all the processes now in vogue.

The Champlevé process seems to have had its origin in Briton, preceding the Roman conquest, thence it passed to France and Italy.

Byzantium and Ireland were long the centers of learning, and in art they were unrivaled for the beauty of their enamels in Cloisonné and Champlevé.

The fine craft of enameling did not assert its independence as an art in its full capacity, for change and progress, until the Twelfth Century.

References.—Although a great deal of enameling on metal is done at present in the manufacture of jewelry, emblems, and buttons, the manipulation or application of enamels, independent of their manufacture and composition, is still considered a trade secret. But, whereas, in

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recent years a few very instructive books have been written on the manipulation and application of enamels upon metals, very little information can be found in literature on the composition, and the effects of the various constituents on the properties of the enamel.

INVESTIGATION.

Object.—This thesis was undertaken to determine the effect of the glass-making constituents in the so-called jewelry enamel.

The first part of this investigation will be the production of a suitable "flux," or colorless transparent enamel, and second, the production of colored enamels, using this flux as a base.

Only transparent enamels were attempted, because any of these may be made opaque by the addition of a small amount of tin oxide, without affecting the other properties.

Metal Used.—The metal used throughout this investigation was copper. The object of working copper was because it is an acknowledged fact that almost all enamels, working well on copper, will do so on gold and silver, though the converse is not true, owing to the relative ease with which copper oxidizes; second, because of the prohibitive cost of gold and silver for extensive experimental work.

The metal trial pieces consisted of No. 20 gauge commercial sheet copper, cut into pieces 1 inch by 2 inches; a small depression about 3/16 inch by 1/2 inch by 1/32 inch deep was cut into each trial, by means of a groover's tool, to keep the enamel confined.

Commercial Fluxes as Standards.—For purposes of comparison, three different commercial fluxes and three-colored enamels were purchased from F. A. Schutt, of Pforzheim, Germany, manufacturer of fine enamels. These were fused onto copper and tested as were the experimental enamels.

Fritting.—The fritting of the experimental batches was done in a Fletcher gas-air furnace, from which the

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muffle had been removed, and a hole cut in the bottom. A small crucible, 2 inches in diameter and 4 inches high, with a 1/4-inch hole in its bottom, was placed in the furnace so that the holes in the crucible and furnace coincided. The furnace was heated by a large gas blast lamp.

The enamel mixes were placed in the crucible, one at a time, and as they melted were granulated by dropping into a pan of water beneath the furnace.

Grinding.—The fritted enamels were ground wet in a small agate mortar to pass a hundred-mesh sieve.

Washing.—The powder was then washed until the water was no longer milky. The fine particles or "mud," it was found, made the enamel gray or cloudy, hence the washing.

Preservation.—The ground enamels were now placed in small vials and labeled, ready for application.

Pickling of the Copper.—The metal pieces were "pickled" or cleaned by dipping them into concentrated nitric acid, then into a strong solution of hot crystal soda to remove all traces of grease, and finally washed in clear water.

Application of Enamels.—The enamel powder was wet up with water to a thick paste and the groove in the copper trials filled with this paste by means of a spatula, and then the whole dried on top of the furnace.

Firing.—The firing was done in a small muffle Buffalo dental furnace, heated by a gas blast lamp and equipped with thermo-electric couple pyrometer. The furnace was heated to 1050° F., as it was found that the soft commercial enamels manufactured by Schutt were completely melted at this temperature in two minutes, this being the time advised by the various writers.

The trial pieces were placed in the muffle on a small porcelain tile by means of tongs, and allowed to remain until perfectly fused, the degree of vitrification being determined by the reflection of a rod held above the piece.

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CLEAR COLORLESS ENAMELS.

Molecular Formula of Published Recipes.—The type formulae given by the various writers for an enamel flux are as follows:

Brown, "Art Enameling on Metal." Molecular formula:

$$\left.\begin{matrix} 0.451\ PbO \\ 0.508\ K_2O \\ 0.0413\ Na_2O \end{matrix}\right\} \begin{matrix} 0.852\ SiO_2 \\ 0.0813\ B_2O_3 \end{matrix}$$

Batch formula:

Silica	18.7%
Minium	37.5
Niter	37.5
Borax	6.2

Fisher, molecular formula:

$$\left.\begin{matrix} 0.371\ PbO \\ 0.629\ K_2O \end{matrix}\right\} 0.706\ SiO_2$$

Batch formula:

Silica	18.2%
Minium	27.3
Niter	54.4

Cunynghome, molecular formula:

$$\left.\begin{matrix} 0.685\ PbO \\ 0.324\ K_2O \end{matrix}\right\} 3.64\ SiO_2$$

Batch formula:

Silica	50%
Minium	35
Niter	15

Basis Chosen.—It will be noted that there is a wide divergence in the above compositions; the formula given by Brown seemed to be the most fusible enamel, consequently, with this formula as a basis, three series of four members each were designed.

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Series A.—In Series A, the ratios of silica, niter, and borax were kept constant, and the white lead increased from 33 per cent. to 44.4 per cent.

Series B.—In Series B the ratios of silica and the borax increased from 6.6 per cent. to 21 per cent.

Series C.—In Series C the ratios of silica, white lead and borax were kept constant, and soda added as calcined Na_2CO_3 being increased at the expense of the niter.

The molecular formulae are as follows:

Series A.

	PbO	K_2O	Na_2O	SiO_2	B_2O_3
(1).....	0.3725	0.579	0.0507	0.965	0.1006
(2).....	0.3944	0.5565	0.0484	0.927	0.0968
(3).....	0.454	0.502	0.0437	0.837	0,0875
(4).....	0.4867	0.471	0.0409	0.785	0.081

Series B.

	PbO	K_2O	Na_2O	SiO_2	B_2O_3
(1).....	0.394	0.556	0.048	0.927	0.0968
(2).....	0.377	0.531	0.094	0.885	0.188
(3).....	0.359	0.507	0.132	0.845	0.264
(4).....	0.344	0.486	0.169	0.810	0.333

Series C.

	PbO	K_2O	Na_2O	(Borax) Na_2O	SiO_2	B_2O_3
(1).....	0.293	0.414	0.222	0.070	0.690	0.14
(2).....	0.254	0.297	0.386	0.0626	0.60	0.125
(3).....	0.224	0.208	0.509	0.055	0.528	0.110
(4).....	0.202	0.141	0.612	0.0496	0.475	0.096

Calculation of Batch Weights.—The batch weights were now calculated from the molecular formulae. For example, in the case of Member 1 of Series A, molecular formula of which is

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$$\left.\begin{array}{l} 0.3725\ PbO \\ 0.579\ K_2O \\ 0.0503\ Na_2O \end{array}\right\} \quad \begin{array}{l} 0.965\ SiO_2 \\ 0.1006\ B_2O_3 \end{array}$$

we have:

			Batch wt.		Factor		Parts by wt.
0.375 PbO	× 258 (eqv. wt. of white lead)	=	96.105	×	0.0518	=	5
0.579 K_2O	× 202 (eqv. wt. of niter)	=	116.958	×	0.0518	=	6
0.965 SiO_2	× 60 (eqv. wt. of silica)	=	57.90	×	0.0518	=	3
0.0503 Na_2O	× 382 (eqv. wt. of borax)	=	19.21	×	0.0518	=	1

Parts by Weight.—The members in each series were calculated in like manner, with the following results in parts by weight:

Series A.

	Silica	White lead	Niter	Borax
(1).....	3	5	6	1
(2).....	3	6	6	1
(3).....	3	7	6	1
(4).....	3	8	6	1

Series B.

	Silica	White lead	Niter	Borax
(1).....	3	6	6	1
(2).....	3	6	6	2
(3).....	3	6	6	3
(4).....	3	6	6	4

Series C.

	Silica	White lead	Niter	Borax	Na_2O
(1).....	3	6	5	2	1
(2).....	3	6	4	2	2
(3).....	3	6	3	2	3
(4).....	3	6	2	2	4

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Mixing.—The above parts were now weighed up in grams and well mixed by hand.

Length of Heating Period.—The prepared trials were found to require the following time for complete vitrification at this temperature (1050° F.):

A—1	70	seconds.
2	70	"
3	90	"
4	100	"
B—1	50	"
2	40	"
3	80	"
4	120	"

None of the members of Series C were fired as it was found that all but C_1 were very soluble, having formed a water glass while standing in water after grinding. C_1 though not quite so markedly soluble was still too soluble for use. The solubility was, no doubt, due to the high ratio of alkali to silica.

RESULTS.

Order of Fusibility.—The order of fusibility was further determined by firing all the members of each series on one trial piece; four of these trials were prepared and each drawn at a different state of vitrification. In Series A, the order was:

A1, A2, A3, A4, and in Series B, the order B2, B1 B3, B4.

It was found that all of these enamels matured with less heat treatment than did the purchased enamels.

Crazing.—The fitting properties were determined by plunging the pieces, red hot, as taken from the muffle, into cold water and examining the resulting enamels under a magnifying glass. The following results were observed:

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A1	crazed badly.
A2	crazed slightly
A3	crazed slightly.
A4	crazed very slightly.
B1	crazed slightly.
B2	crazed badly.
B3	crazed badly.
B4	cracked off of the metal.

The two softer commercial enamels crazed slightly with this treatment but the harder one remained perfect.

Durability.—The durability was determined by placing the trials under a bell jar over concentrated fuming hydrochloric acid, and allowing the acid fumes to act upon the enamels for 24 hours. The following results were observed:

A1	completely decomposed.
A2	completely decomposed.
A3	completely decomposed.
A4	completely decomposed.
B1	completely decomposed.
B2	very dull and rough.
B3	dull and rough.
B4	matt.

The commercial enamels were all glossy after this treatment.

CONCLUSIONS ON SERIES A, B AND C.

Series A.—With an increase in PbO from 0.37 to 0.49 equivalent with a corresponding decrease in the other constituents, we find that

1. The enamels become less fusible.
2. The tendency toward crazing decreased.
3. All were decomposed by HCl fumes.

Series B.—With an increase in borax from 0.097 to 0.338 equivalent B_2O_3, and a corresponding decrease in the other constituents, we find that

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1. The most fusible mixture contains 0.188 equivalent B_2O_3 (B2) and that above and below this amount the enamel becomes less fusible.

2. The crazing becomes more pronounced with increase of B_2O_3; even with the smallest amount of B_2O_3 (0.097 equivalent), crazing is very evident.

3. The action of hydrochloric acid fumes becomes less pronounced.

Series C.—With this content of Na_2O and SiO_2, we find that the enamels are too soluble in water to be of use.

SUMMARY.

We find, then, that although a very low fusing enamel has been produced, the durability has of necessity been somewhat sacrificed. It is evident that the tests to which the trials have been subjected are much more severe than those met in every-day use; still, a well-executed piece of enamel requires so much skill and time that the result should stand any possible conditions without danger.

It seems advisable, therefore, to make a more durable enamel, even at the expense of the low fusibility, if necessary. With this idea in view, the following series were designed:

SERIES D, E AND F.

No borax was used as this seems to promote crazing. The silica was kept constant in each series, with an increase in K_2O and a corresponding decrease in PbO.

Series D.—Molecular formulae:

	K_2O	PbO	SiO_2
(1)	0.2	0.8	2.0
(2)	0.3	0.7	2.0
(3)	0.4	0.6	2.0
(4)	0.5	0.5	2.0
(5)	0.6	0.4	2.0
(6)	0.7	0.3	2.0

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The batch weights, in each case, were calculated as before with the following result, parts by weight.

	Niter	White lead	Silica
(1).....	4.0	20.6	12.0
(2).....	6.0	18.06	12.0
(3).....	8.0	15.5	12.0
(4).....	10.0	12.9	12.0
(5).....	12.0	10.3	12.0
(6).....	14.0	7.7	12.0

Series E.—Molecular formulae:

	K_2O	PbO	SiO_2
(1).....	0.2	0.8	1.5
(2).....	0.3	0.7	1.5
(3).....	0.4	0.6	1.5
(4).....	0.5	0.5	1.5
(5).....	0.6	0.4	1.5
(6).....	0.7	0.3	1.5

Batch formulae in parts by weight:

	Niter	White lead	Silica
(1).....	4.0	20.6	9.0
(2).....	6.0	18.06	9.0
(3).....	8.0	15.5	9.0
(4).....	10.0	12.9	9.0
(5).....	12.0	10.3	9.0
(6).....	14.0	7.7	9.0

Series F.—Molecular formulae:

	K_2O	PbO	SiO_2
(1).....	0.2	0.8	1.0
(2).....	0.3	0.7	1.0
(3).....	0.4	0.6	1.0
(4).....	0.5	0.5	1.0
(5).....	0.6	0.4	1.0
(6).....	0.7	0.3	1.0

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Batch formulae in parts by weight:

	Niter	White lead	Silica
(1).....	4.0	20.6	6.0
(2).....	6.0	18.06	6.0
(3).....	8.0	15.5	6.0
(4).....	10.0	12.9	6.0
(5).....	12.0	10.3	6.0
(6).....	14.0	7.7	6.0

Firing.—The enamels were fritted, ground, washed and applied as in the case of Series A, B and C. The firing was done at a somewhat higher temperature, keeping the time of firing about two minutes.

RESULTS.

Fusibility.—The order of fusibility was determined as before, and found to be as follows, being in the same order in each series: From most fusible to least fusible, 1, 2, 3, 4, 5, and 6. It was noticed that Nos. 1, 2, and 3 in each series fused sooner than Nos. 4, 5 and 6, that is, there was a greater step between Nos. 3 and 4 than between any of the others.

Series F was the most fusible, and Series E and D the most refractory. Members 1, 2 and 3 of Series F fused with the same heat treatment as the softest of the purchased enamels.

Fit.—All members of Series D and E fit perfectly when dipped, red hot, into cold water. In Series F, Members 1, 2 and 3 fit with this treatment while Members 4, 5 and 6 crazed slightly.

Durability.—When subjected to hydrochloric acid fumes, as described before, all members of Series D remained perfectly bright. In Series E, Members 1, 2 and 3 became dull, while Members 4, 5 and 6 remained bright. In Series F, Members 1, 2, 3 and 4 were dull, while Members 5 and 6 remained bright.

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Luster.—It was noted that the high lead enamels of each series were brighter or showed more refractive power than those low in PbO.

GENERAL CONCLUSIONS.

1. **Effect of SiO_2.**—With an increase in SiO_2 the enamels became less fusible though more permanent and durable. 1.0 equiv. SiO_2 was found too low for durability, and 2.0 equiv. too high for a soft enamel.

2. **Effect of PbO.**—With an increase in PbO, and a corresponding decrease in K_2O, with the same SiO_2 content, the enamels

a. Became more fusible.

b. Have a decreased tendency to craze.

c. Became more refractive.

d. Are less durable in the acid fumes.

3. Members 4, 5 and 6 of Series E were found to compare very favorably with the purchased enamels, in all respects.

SERIES G, H, I AND J.

Though the original object in view, the production of a suitable flux, had been accomplished, it was thought advisable to make up three more series to determine the effect of an addition of Al_2O_3, CaO and borax, with a higher SiO_2 content.

Accordingly, the following series were made up, Member 4 of Series E being taken as the basis in each case.

Series G.—In this series the ratio of K_2O to PbO was kept constant, and B_2O_3 increased; the resulting molecular formulae are as follows:

	PbO	K_2O	Na_2O	SiO_2	B_2O_3
(1).....	0.487	0.487	0.025	1.725	0.05
(2).....	0.475	0.475	0.050	2.00	0.1
(3).....	0.462	0.462	0.075	2.17	0.15
(4).....	0.450	0.450	0.100	2.40	0.2

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When calculated to batch weights as described before, the following formulae in parts by weights were obtained:

	White lead	Niter	Silica	Borax
(1).....	12.6	9.84	10.35	1.9
(2).....	12.2	9.6	12.0	3.8
(3).....	11.9	9.3	12.9	5.7
(4).....	11.6	9.1	14.4	7.6

RESULTS.

When the enamels were weighed, fused, ground, applied and tested as before, the following results were obtained:

(*a*) With an increase in borax:

1. Fusibility increased, though not very markedly.

2. Tendency to craze was increased, Member 1 fitting, and Members 2, 3 and 4 crazing.

(*b*) All members were matt after the fuming acid treatment, the roughness being more noticeable with the higher borax.

Series H.—In this series the ratios of PbO, K_2O, and SiO_2 to each other were kept constant and Al_2O_3 increased from 0.025 equiv. to 0.1 equiv.

The molecular formulae are as follows:

	PbO	K_2O	Al_2O_3	SiO_2
(1).....	0.5	0.5	0.025	1.5
(2).....	0.5	0.5	0.050	1.5
(3).....	0.5	0.5	0.075	1.5
(4).....	0.5	0.5	0.100	1.5

The Al_2O_3 was added as dehydrated Al_2O_3, giving the following batch formulae in parts by weight:

	White lead	Niter	Al_2O_3	SiO_2
(1).....	12.9	10.0	0.025	9.0
(2).....	12.9	10.0	0.050	9.0
(3).....	12.9	10.0	0.075	9.0
(4).....	12.9	10.0	0.100	9.0

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In fritting this series, it was found that Members 3 and 4 were too viscous to flow through the crucible and Members 1 and 2, while flowing through the crucible, were too viscous to be used as enamels. Hence discarded.

Series J.—Another series, J, was therefore, designed with the same molecular formulae and equivalents of Al_2O_3, but having the Al_2O_3 added as china clay, with the following formulae in parts by weight:

	White lead	Niter	Clay	Silica
(1).....	6.5	5.0	0.33	4.35
(2).....	6.5	5.0	0.65	4.20
(3).....	6.5	5.0	0.97	4.05
(4).....	6.5	5.0	1.29	3.90

This series was then weighed, fritted, ground, applied and tested as before.

RESULTS.

With the increase in Al_2O_3 content from 0.025 to 0.1 equiv.:

1. Fusibility was decreased; all members were very viscous, those high in Al_2O_3 requiring an exceedingly long and high heat treatment to become smooth.
2. The tendency toward devitrification was increased.
3. All were slightly crazed.
4. With the fuming acid treatment, Members 1 and 2 remained glossy while Members 3 and 4 were slightly dulled.

Series I.—In this series the K_2O and SiO_2 were kept constant and CaO increased at the expense of the PbO.

The molecular formulae were as follows:

	PbO	CaO	K_2O	SiO_2
(1).....	0.4	0.1	0.5	1.5
(2).....	0.3	0.2	0.5	1.5
(3).....	0.2	0.3	0.5	1.5
(4).....	0.1	0.4	0.5	1.5

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Batch formulae in parts by weight:

	White lead	Whiting	Niter	Silica
(1).....	10.7	1.0	10.0	9.0
(2).....	7.79	2.0	10.0	9.0
(3).....	5.16	3.0	10.0	9.0
(4).....	2.58	4.0	10.0	9.0

This series when fritted, ground, applied and tested as before, gave the following results:

With an increase in CaO,

1. The fusibility decreased.

2. Crazing increased, though all were crazed to a more or less extent.

3. All were slightly affected by the acid fumes.

Series K.—In this series zinc oxide was added at the expense of the PbO and K_2O, keeping the SiO_2 constant.

The molecular formulae are as follows:

	PbO	K_2O	ZnO	SiO_2
(1).....	0.487	0.487	0.025	1.5
(2).....	0.475	0.475	0.05	1.5
(3).....	0.462	0.462	0.075	1.5
(4).....	0.450	0.450	0.100	1.5

Giving the following formulae in parts by weight:

	White lead	Niter	ZnO	SiO_2
(1).....	12.6	9.83	0.203	9.0
(2).....	12.2	9.6	0.406	9.0
(3).....	11.9	9.3	0.609	9.0
(4).....	11.6	9.1	0.812	9.0

RESULTS.

This series when fritted, ground, applied and tested as before, gave the following results:

With an increase in ZnO,

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1. The fusibility decreased.

2. Crazing increased, Members 1, 2 and 3 fitting perfectly, while Member 4 crazed.

3. Tendency toward devitrification increased.

4. None were affected by the acid fumes.

COMPARISON OF SERIES.

The melting points of the *most* fusible members of each series were now compared and found to be as follows: In order from least fusible to most fusible, J1, I1, K1, G_4, and E_4.

We find then that in no case have we increased the fusibility, and although the durability has been somewhat bettered in some cases, yet the crazing has increased in such cases to make the enamel undesirable.

We find then that the best soft enamel flux found in this investigation is a high lead flint glass of the following compos tion,

$$\left.\begin{matrix} 0.5\ PbO \\ 0.5\ K_2O \end{matrix}\right\} 1.5\ SiO_2\ (E\ 4),$$

and that this flux compares favorably in every way with the commercial soft flux examined.

For a hard, flux enamel, we find a glass of the same R O. elements, but a higher SiO_2 content, with the following formula to be very suitable:

$$\left.\begin{matrix} 0.5\ PbO \\ 0.5\ K_2O \end{matrix}\right\} 2.0\ SiO_2\ (D_4)$$

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A COMPARISON OF COMMERCIAL GROUND COATS FOR CAST IRON ENAMELS.

By JOHN H. COE, Mansfield, Ohio.[1]

INTRODUCTION.

Purpose.—The writer has, in these experiments, attempted to compare the different types of commercial ground coats now in use, as to their heat range and ability to bond the enamel.

Definition.—A ground coat may be defined as a very thin, transparent glaze applied to cast iron articles not only to act as a bond between the white, opaque enamel and the cast iron, but to prevent the iron from oxidizing while being raised up to the temperature at which the enamel fuses. It should have the following properties:

1. It should begin to fuse at dull red heat and remain a good glass through a considerable heat range.
2. It should be able to dissolve any oxide or foreign matter on the surface of the metal.
3. Its viscosity should be very low.
4. It should not contain or absorb injurious gases, such as sulphur.

The Literature.—The following is practically the full extent of the literature on this subject:

1. Paul Randau, "Enamels by Wet Method."
2. M. B. Cheney,
Thesis at The Ohio State University, "Composition."
3. Dillen Underhill, *Foundry Magazine*, March, 1910, "Materials."
4. H. F. Staley, Vol. VIII, *Trans. A. C. S.*, "Methods."
5. Von R. Vondracek, *Sprechsaal*, Nos. 14 and 15, 1909, "Materials and Methods."
6. L. Petrik, (*a*) *Mon. Ceram.*, 1892, No. 21, p. 199. (*b*) *Die Tonwaren Industrie*, 1908.
7. F. H. Riddle, Vol. IX, *Trans. A. C. S.*, "Cover Enamels."

[1] Done as a thesis under the direction of Homer F. Staley, Ohio State University.

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There are many classes of ground coats, but an examination of successful recipes will show that the great majority contain borax, red lead and nitrate of sodium.

The value of each of these ingredients is as follows:

(*a*) Boric acid from the borax readily dissolves any metallic oxides.

(*b*) Na_2O and PbO are low temperature fluxes and have not as great a tendency to absorb sulphur gases as has the other available fluxing materials.

(*c*) The PbO should be added as red lead as the escaping oxygen is desirable in preventing the injurious gases in the fritt kiln from entering the ground coat.

THE INVESTIGATION.

Since the commercial ground coats vary widely, not only in composition but also in the proportion of fritted to raw ingredients, this investigation was so planned as to cover both of these. The general outline is given in Table I.

Table I.

Classes	Groups	Series	Sub series
A All fritted.	I. Without cobalt.	(*a*) Single glasses.	(1) Flint glass. (2) Feldspar glass. (3) Clay glass.
		(*b*) Blends of glasses.	(1) Blends of two glasses. (2) Blends of three glasses.
	II. With 1 per cent. cobalt oxide.	Same as above.	Same as above.
	I. One fritt, one raw material.	(*a*) Flint fritt. (*b*) Feldspar fritt.	(1) Raw feldspar. (2) Raw flint. (3) Raw clay.

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Table I (*Continued*).

Classes	Groups	Series	Sub series
B Part fritted, part raw.	II. One fritt, blends of raw materials.	(*c*) Clay fritt.	
		(*a*) Flint fritt.	(1) Blends of two raw materials.
		(*b*) Feldspar fritt.	
		(*c*) Clay fritt.	(2) Blends of three raw materials.
	III. Blended fritts, one raw material.	(*a*) Raw feldspar.	(1) Blends of two fritts.
		(*b*) Raw flint.	(2) Blends of three fritts.
		(*c*) Raw clay.	
C All raw.			(1) Refractory material feldspar.
			(2) Refractory material flint.
			(3) Refractory material clay.

Material Used.—Since the proportion of borax, white lead and sodium nitrate was kept constant in all the ground coats, whether fritted or raw, these materials in the proportions used, will be known as the "Constant Group."

Borax	15
White lead[1]	20
Sodium nitrate	2

The other materials were:

Brandywine feldspar
Mayfield ball clay
American flint

The ratio of flint feldspar and clay that can be interchangeably substituted in a given mixture without changing its fusion point was taken as being approximately as

[1] White lead was used rather than red lead for the latter was not available.

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100 parts by weight of feldspar
65 parts by weight of flint
40 parts by weight of clay

The above-mentioned amounts of feldspar, flint and clay were fritted with the "Constant Group" to form the "Single Glasses" of Class A, Group I. The remaining members of Class A, Group I were made from blends of these glasses.

The same procedure was followed in Class A, Group II, except that 0.1 per cent. of Co_3O_4 was added to the raw batch of each of the "Single Glasses."

In Class B, since part of the hardening material was to be added raw, the total amount was reduced. Three fritts were made up consisting in each case of the "Constant Group" and one of the following amounts of hardening materials: Flint 25, feldspar 40, clay 16. To these were added, to make the various members of Group I, the following amounts of hardening materials: Flint 31, feldspar 52, clay 21. The remaining members of Class B were made from blends of these.

The members of Class C being all raw, the amounts of hardening materials were still further reduced to flint 52, feldspar 80, clay 32.

In making blends, the following proportions were used in all cases:

Two Extremes.

$^2/_3$	$^1/_3$
$^1/_2$	$^1/_2$
$^1/_3$	$^2/_3$

Three Extremes.

$^1/_3$	$^1/_3$	$^1/_3$
$^1/_2$	$^1/_4$	$^1/_4$
$^1/_4$	$^1/_2$	$^1/_4$
$^1/_4$	$^1/_4$	$^1/_2$

Procedure.—The ground coats were mixed with just enough water to give them a creamy consistency, then

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applied by dipping. Immediately after dipping, the trials were placed on top of the furnace where they would dry quickly and when dry they were at once placed in the furnace. The temperature was approximately 1800° F. when the dried trials were placed in the furnace, but it dropped to about 1500° F. and then gradually rose again as the trial gathered heat.

The time between fusion and volatilization of the ground coats is given in Table II, together with the heat range of the different coats.

All coats having a heat range of 200° F. or over were set aside to be used under a standard enamel. These coats were applied as before and when the temperature had risen 150° F., above the fusing point of the ground coat, the trial was taken out and without allowing it to cool below red heat, a coat of the standard enamel was dusted on through a forty-mesh sieve. It was then replaced in the furnace and caused to remain there until the enamel was thoroughly fused. A second coat was then applied, the trial again placed in the furnace and heated until the enamel flowed evenly on the trial. The trial was removed and allowed to cool at room temperature.

The Furnace Used.—The furnace used was a simple up-draft muffle furnace. The trials were supported on two parallel iron rods. Directly beneath the rods was an unprotected thermo-electric couple for measuring the temperatures of the furnace.

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Table II.

Class A. All Fritted.

Group I. Containing no cobalt.

		Fritted					Raw			Heat range	
		Serial No.	Constant group	Flint	Feldspar	Clay	Flint	Feldspar	Clay	Temp. range, deg. F.	Time, minutes
Single glasses		101	37	65	...	..	....	.....	.....	150	15
		102	37	..	100	..	....	.....	.....	158	20
		103	37	..	...	40	....	.....	.....	100	20
Blends of two glasses	Flint and feldspar	111	37	44	33	..	....	.....	.....	200	20
		112	37	33	50	..	....	.....	.....	225	20
		113	37	22	66	..	....	.....	.....	225	20
	Flint and clay	114	37	44	...	13	....	.....	.....	175	20
		115	37	33	...	20	....	.....	.....	130	20
		116	37	22	...	26	....	.....	.....	150	20
	Feldspar and clay	117	37	..	66	13	....	.....	.....	125	20
		118	37	..	50	20	....	.....	.....	100	15
		119	37	..	33	26	....	.....	.....	100	20
Blends of three glasses		121	37	22	33	13	....	.....	.....	120	20
		122	37	32	25	10	....	.....	.....	185	30
		123	37	16	50	10	....	.....	.....	190	30
		124	37	16	25	20	....	.....	.....	100	15

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Class A. All Fritted (*Continued*).

Group II. Containing 1 Per cent. Cobalt Oxide in the Fritt.

			Fritted				Raw			Heat range	
		Serial No.	Constant group	Flint	Feldspar	Clay	Flint	Feldspar	Clay	Temp. range, deg F.	Time, minutes
Single glasses		201	37	65	...	..	....	....	.....	100	14
		202	37	..	100	..	....	....	.....	150	17
		203	37	..	...	40	....	....	.....	140	17
Blends of two glasses	Flint and feldspar	211	37	44	33	..	....	....	.....	220	25
		212	37	33	50	..	....	....	.....	150	20
		213	37	22	66	..	....	....	.....	225	25
	Flint and clay	214	37	44	...	13	....	....	.....	75	5
		215	37	33	...	20	....	....	.....	95	12
		216	37	22	...	26	....	....	.....	95	12
	Feldspar and clay	217	37	..	66	13	....	....	.....	75	11
		218	37	..	50	20	....	....	.....	25	7
		219	37	..	33	26	....	....	.....	25	5
Blends of three glasses		221	37	22	33	13	....	....	.....	95	7
		222	37	32	25	10	....	....	.....	90	6
		223	37	16	50	10	....	....	.....	100	10
		224	37	16	25	20	....	....	.....	100	10

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Class B. Part Fritted, Part Raw.

Group I. One Fritt, One Raw Material.

	Serial No.	Fritted material				Raw material			Heat range	
		Constant group	Flint	Feldspar	Clay	Flint	Feldspar	Clay	Temp. range, deg. F.	Time, minutes
Flint fritt	301	37	25	..	..	31	..	..	145	10
	302	37	25	..	..	..	52	..	150	10
	303	37	25	..	..	..	..	21	120	5
Feldspar fritt	304	37	..	40	..	31	..	..	200	10
	305	37	..	40	..	..	52	..	175	12
	306	37	..	40	..	..	..	21	125	5
Clay fritt	307	37	..	..	16	31	..	..	145	7
	308	37	..	..	16	..	52	..	140	9
	309	37	..	..	16	..	..	21	100	10

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Class B. Part Fritted, Part Raw (*Continued*).

Group II. One Fritt, Two Raw Materials.

	Fritted material					Raw materials			Heat range	
	Serial No.	Constant group	Flint	Feldspar	Clay	Flint	Feldspar	Clay	Temp. range, deg. F.	Time, minutes
Flint fritt	401	37	25	..	..	20	17	..	135	10
	402	37	25	..	..	16	26	..	140	12
	403	37	25	..	..	10	34	..	135	10
	404	37	25	..	..	20	..	7	130	6
	405	37	25	..	..	16	..	10	140	6
	406	37	25	..	..	10	..	14	140	10
	407	37	25	..	..	..	34	7	160	13
	408	37	25	..	..	..	26	10	150	8
	409	37	25	..	..	..	17	14	115	10
Feldspar fritt	411	37	..	40	..	20	17	..	200	17
	412	37	..	40	..	16	26	..	200	17
	413	37	..	40	..	10	34	..	225	17
	414	37	..	40	..	20	..	7	150	13
	415	37	..	40	..	16	..	10	140	12
	416	37	..	40	..	10	..	14	100	6
	417	37	..	40	..	..	34	7	130	5
	418	37	..	40	..	..	26	10	150	8
	419	37	..	40	..	..	17	14	150	8

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Class B. Part Fritted, Part Raw (*Continued*).

	Fritted material					Raw materials			Heat range	
	Serial No.	Constant group	Flint	Feldspar	Clay	Flint	Feldspar	Clay	Temp. range, deg. F.	Time, minutes
Clay fritt	421	37	..	..	16	20	17	..	150	8
	422	37	..	..	16	16	26	..	160	9
	423	37	..	..	16	10	34	..	160	9
	424	37	..	..	16	20	..	7	105	7
	425	37	..	..	16	16	..	10	115	8
	426	37	..	..	16	10	..	14	105	7
	427	37	..	..	16	..	24	7	125	8
	428	37	..	..	16	..	26	10	115	6
	429	37	..	..	16	..	17	14	115	6

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Class B. Part Fritted, Part Raw (*Continued*).

Group III. One Fritt, Three Raw Materials.

		Fritted material				Raw materials			Heat range	
	Serial No.	Constant group	Flint	Feldspar	Clay	Flint	Feldspar	Clay	Temp. range, deg. F.	Time, minutes
Flint fritt	501	37	25	..	..	17	10	7	145	19
	502	37	25	..	..	16	13	5	140	13
	503	37	25	..	..	8	26	5	125	13
	504	37	25	..	..	8	13	10	145	19
Feldspar fritt	511	37	..	40	..	17	10	7	115	12
	512	37	..	40	..	16	13	5	125	14
	513	37	..	40	..	8	26	5	115	12
	514	37	..	40	..	8	13	10	125	14
Clay fritt	521	37	..	..	16	17	10	7	115	7
	522	37	..	..	16	16	13	5	105	6
	523	37	..	..	16	8	26	5	110	6
	524	37	..	..	16	8	13	10	105	6

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Class B. Part Fritted, Part Raw (*Continued*).

Group. IV. Two Fritts, One Raw Material.

		Fritted materials					Raw material			Heat range	
	Serial No.	Constant group	Flint	Feldspar	Clay	Flint	Feldspar	Clay	Temp. range, deg. F	Time, minutes
Flint and feldspar fritts	601	37	16	13	..	31	..	..	180	14
	602	37	12	20	..	31	..	..	175	13
	603	37	8	26	..	31	..	..	200	15
	604	37	16	13	..	..	52	..	225	20
	605	37	12	20	..	..	52	..	200	12
	606	37	8	26	..	..	52	..	225	20
	607	37	16	13	..	..	..	21	195	20
	608	37	12	20	..	..	..	21	190	20
	609	37	8	26	..	..	..	21	210	20
Flint and clay fritts	611	37	16	..	5	31	..	..	130	15
	612	37	12	..	8	31	..	..	135	17
	613	37	8	..	10	31	..	..	130	15
	614	37	16	..	5	..	52	..	175	15
	615	37	12	..	8	..	52	..	175	15
	616	37	8	..	10	..	52	..	175	15
	617	37	16	..	5	..	..	21	175	10
	618	37	12	..	8	..	..	21	150	7
	619	37	8	..	10	..	..	21	150	7
Feldspar and clay fritts	621	37	..	26	5	31	..	..	150	15
	622	37	..	20	8	31	..	..	150	15
	623	37	..	13	10	31	..	..	140	13
	624	37	..	26	5	..	52	..	175	17
	625	37	..	20	8	..	52	..	175	17
	626	37	..	13	10	..	52	..	125	10
	627	37	..	26	5	..	..	21	160	20
	628	37	..	20	8	..	..	21	150	17
	629	37	..	13	10	..	..	21	150	17

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Class B. Part Fritted, Part Raw (*Continued*).

Group V. Three Fritts, One Raw Material.

	Serial No.	Fritted materials				Raw material			Heat range	
		Constant group	Flint	Feldspar	Clay	Flint	Feldspar	Clay	Temp. range, deg. F.	Time, minutes
Three fritts. Raw flint	701	37	8	13	5	31	..	..	125	21
	702	37	12	10	4	31	..	..	225	30
	703	37	6	20	4	31	..	..	225	30
	704	37	6	10	8	31	..	..	100	10
Three fritts. Raw feldspar	711	37	8	13	5	..	52	..	250	20
	712	37	12	10	4	..	52	..	240	18
	713	37	6	20	4	..	52	..	250	20
	714	37	6	10	8	..	52	..	225	15
Three fritts. Raw clay	721	37	8	13	5	..	..	21	175	17
	722	37	12	10	4	..	..	21	190	20
	723	37	6	20	4	..	..	21	200	21
	724	37	6	10	8	..	..	21	175	17

Class C. All Raw.

Serial No	Raw materials				Heat range	
	Constant group	Flint	Feldspar	Clay	Temp. range, deg. F.	Time, minutes
801	37	52	..	..	175	25
802	37	..	..	..	175	25
803	37	..	80	32	160	20

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DISCUSSION ON HEAT RANGE.

Class A. All Fritted.

Group I. Containing No Cobalt.

Single Glasses.—No one of these has a wide heat range. The flint and feldspar glasses are about equal while the glass containing clay has a much shorter heat range.

Blends of Two Glasses.—In the case of blends of the flint and feldspar glasses, we have a marked improvement in width of heat range over single glasses. While the flint glass alone has a range of 150° F. and the feldspar of 158° F., blends of these glasses give heat ranges of 200° to 225°.

In mixtures of flint glass with clay glass, we get all values higher than for the clay glass alone, and with high flint, higher than for the flint glass alone.

In blends of clay glass with feldspar glass, all the values are low, the best value being with the highest content of feldspar glass.

Blends of Three Glasses.—In these we find the highest values where the clay glass is lowest. These values are higher than those for single glasses, and for blends of clay glass with one other glass, but not as high as for blends of two glasses, neither of which is a clay glass.

This group of ground coats shows:

1. Other things being equal, a blend of two glasses is better than one glass, and of three glasses, better than two.
2. Clay is not a suitable material to use in a glass if a long heat range is desired.
3. Flint and feldspar glasses of equal fusibility have about the same heat range.

Group II. Containing 1 Per cent. Cobalt Oxide in the Fritt.

As this group was of the same composition as Group I, with the exception that each member of Group II contains 0.1 per cent. cobalt oxide, any difference in heat range may be attributed to this substance. We find that as a

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general proposition the poor and medium grade ground coats had their heat range shortened by the addition of the cobalt, while the best compositions were not injured and in one case (No. 211) the heat range seems to have been slightly extended.

We draw the following conclusion:

The use of cobalt in a ground coat for cast iron enamels is of doubtful value.

Class B. Part Fritted, Part Raw.

Group I. One Fritt, One Raw Material.

In these we find:

1. The feldspar fritt gives longest heat range, flint fritt gives the next longest, and clay fritt gives the shortest.

2. Clay used as a raw material gives a shorter heat range than either feldspar or flint. With a flint fritt, feldspar, as raw material, gives the best results, while conversely with a feldspar frit, flint, as a raw material, gives the best results.

Group II. One Fritt, Two Raw Materials.

Flint Fritt.—In these we find no coat of long heat range. The values run rather uniform, being about what would be expected from mixtures of coats made up of flint fritt with the various raw materials.

Feldspar Fritt.—When using a feldspar fritt and two raw materials, blends of raw feldspar and flint gave ground coats of considerably longer heat range than blends of raw feldspar and clay or raw flint and clay. In fact these values were the highest obtained by the use of one fritt.

Clay Fritt.—Clay again shows its inferiority as a material for use in the fritt by giving values that run low. The best are found with mixtures of feldspar and flint as raw materials.

Group III. One Fritt, Three Raw Materials.

The heat ranges of the mixtures containing flint and clay fritts are about the same as when using two raw materials. The heat ranges of the mixtures containing

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feldspar fritt are lower than the group in which raw feldspar and flint only are used, *i. e.*, a substitution of clay for feldspar and flint reduced the heat range.

Conclusions for Groups II and III.

1. There is no especial advantage in blending raw materials. The values obtained correspond roughly to the rule of mixtures, *i. e.*, are what would be calculated from the heat ranges of the extremes from which the blends were made.

2. In these groups we have emphasis laid on the fact that clay is a very poor material to use in a fritt and is not as desirable from the standpoint of heat range as flint or feldspar for a raw material.

Group IV. Two Fritts, One Raw Material.

In these we find that there is a decided advantage in blending fritts. Keeping the raw material the same, a coat made up with two fritts in nearly every case has a longer heat range than either of the coats from which it is made up.

Group V. Three Fritts, One Raw Material.

The advantage of blending fritts is here further exemplified. The addition of a material so poor in itself, as clay fritt, to a coat containing two other fritts, gives a longer heat range to the resulting blend.

Class C. All Raw.

The heat ranges in this class are all comparatively short. Little or no advantage could be expected from blending these and so blends were not attempted.

TEST OF RELATIVE BONDING POWER OF THE BEST GROUND COATS.

After considering several methods whereby we could determine which of these ground coats furnished the best

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bond between the iron and the enamel, we resorted to hammering the trial pieces with an ordinary one and a half pound hammer. The Page machine was tried and found inefficient for this, and the time at our disposal was too short to construct a heavier machine after the Page type.

This test is not one to determine the elasticity of the coat or of the enamel but rather the resistance to shelling or flaking when subjected to an impact blow.

No coat which had a heat range of less than 200 degrees F. was tested. Those which were selected for this test were applied to the wedge-shaped cast iron test piece, before described, and then covered with the standard enamel which we have used throughout this investigation.

The enameled trial piece was held firmly on a block that was so substantial as not to cushion the blows from the hammer, and then hammered until a place was found on the trial piece where the bond between the enamel and the coat would break more readily than would the bond between the ground coat and the iron.

None of the trials stood this test on the thinner portion of the trial pieces, but where the piece was more than 3/16 inch thick, the majority of those tested proved to be able to withstand rupture (see Table III).

The reasons for the failure of these ground coats to resist rupturing under this impact test on the thin edge of the trials may in part be:

1. The thin ends had cooled too rapidly to permit of annealing.

2. It is difficult to fuse the ground coat on the heavy end without overburning that which is on the thin end of the trial piece.

3. The thin end vibrates more when being pounded.

The results of this test are tabulated in the following:

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Table III.

Tests of relative bonding power of coats having heat ranges of 200° F. or over.

Serial number	Fraction of whole area laid bare	Style of fracture
111	1/2	Conchoidal
112		Not tested
113	1/2	Conchoidal
211	1/2	Conchoidal
213	1/2	Conchoidal
304		Not tested
411	2/5	Conchoidal
412	1/2	Conchoidal
413	1/2	Perpendicular
603	1/2	Perpendicular
604	1/2	Perpendicular
605	1/2	Perpendicular
606	2/3	Conchoidal
609	All	
702	1/2	Perpendicular
703	1/2	Perpendicular
711		Not tested
712	1/2	Perpendicular
713	1/2	Perpendicular
714	1/2	Conchoidal
723	All	

Conclusions on Tests of Relative Bonding Power.

The tests given were quite severe, and with the exception of those for No. 609 and No. 723 the results would indicate good bonding power. It is worthy of note that in these two compositions, clay was the only raw material. That the rest of the coats show so little difference in bonding power seems to show that almost any ground coat of wide heat range will have good bonding power if heated to a medium point in its heat range.

GENERAL CONCLUSIONS.

The salient points that stand out as a result of this work are:

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1. The use of cobalt oxide in ground for cast iron enamels is of doubtful value.

2. Clay is a very poor material to use in a fritt and is not as desirable as a raw material from the standpoint of heat range, as is feldspar or flint.

3. There is no especial advantage in respect to heat range, in making blends of the materials which are to be used raw.

4. There is a decided advantage in blending fritts as the heat range is thus materially extended.

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PORCELAIN GLAZES.[1]

By Ross C. Purdy, Columbus, O.

INTRODUCTION.

Definition.

Porcelain Glazes are mixtures consisting of ball and china clay, feldspar, flint and some strongly active fluxing material or materials, such as $CaCO_3$, $MgCO_3$, ZnO, $BaCO_3$, $Ca_3(PO_4)_2$ and $CaSO_4 \cdot 10H_2O$.

For the very hardest fired (cones 12–14) porcelains, the flux consists of such eutectics as would be formed by fusing $CaCO_3$ with clay, feldspar and flint.

For the medium fired (cones 8–12) porcelains, ZnO is added to increase the fusibility of the glaze flux. The other materials above mentioned are used at times but not so frequently or to as good advantage as ZnO and $CaCO_3$.

Terra Cotta Glazes are derivatives from the type porcelain glaze but are rendered more fusible (cones 5–8) by approximating more closely the most fusible mixture of clay, feldspar, flint, calcium carbonate and zinc oxide.

Terra cotta glazes are clear or opaque. If used over a white engobe they are designed to be more translucent than when used directly on fire clay bodies.

The two conditions in manufacture of terra cotta that make necessary the development of a mixture somewhat different from those of the porcelain glazes are:

1. Lower heat treatment to mature the body.
2. Necessity of making a white opaque covering to a colored burning body composed of iron-bearing clays.

When white engobes are used, the glaze must have the required fusibility, but need not be as opaque as if it were to be applied directly onto the body clay.

Stoneware Glazes of the bristol type are similar to the terra cotta glazes but are so constituted as to be sufficiently opaque to hide the color of the body without the aid of

[1] The study here reported was made with the senior class at the Ohio State University. The study was made first by the class of '10 and repeated with new mixes by the class of '11. All weighings, etc., were made by two members of the class employed for that purpose. The report as here presented is a copy of the class report.

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an engobe. This requirement calls for the use of what is popularly known as an opacifier. Zinc and tin oxides are the materials most used to develop opacity. Bone ash, fluorspar and zirconium[1] have been used with very limited success.

Typical Formulae.

Hard Fire Porcelain (cone 12–14). See Hainbach, "Pottery Decoration," p. 80.

$$\left.\begin{matrix}0.8\ CaO\\0.2\ K_2O\end{matrix}\right\}\ 0.8\ Al_2O_3\ 4.4\ SiO_2$$

$$\left.\begin{matrix}0.7\ CaO\\0.3\ K_2O\end{matrix}\right\}\ 0.8\ Al_2O_3\ 8.0\ SiO_2$$

Medium Fire Porcelain (cone 8–12).

$$\left.\begin{matrix}0.35\ CaO\\0.25\ K_2O\\0.40\ ZnO\end{matrix}\right\}\ 0.475\ Al_2O_3\ 4.15\ SiO_2$$

used on one fire ware.

$$\left.\begin{matrix}0.7\ CaO\\0.3\ K_2O\end{matrix}\right\}\ 0.5\ Al_2O_3\ 4.0\ SiO_2$$

used on biscuited ware.

Terra Cotta Glaze.—See Parmelee, *Trans. A. C. S.*, Vol. IX.

$$\left.\begin{matrix}0.1–0.7\ CaO\\0.5–0.2\ K_2O\\0.4–0.1\ ZnO\end{matrix}\right\}\ 0.55\ Al_2O_3\ 3.3\ SiO_2$$

Stoneware Bristol Glaze.—See Purdy, *Trans. A. C. S.*, Vols. IV and V.

$$\left.\begin{matrix}0.3–0.15\ CaO\\0.30–0.45\ K_2O\\0.4\ –0.4\ \ ZnO\end{matrix}\right\}\ 0.55\ Al_2O_3\ 3.00\ SiO_2$$

[1] See Sprechsaal, 40, 617 (1907)

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References

"Stoneware Glazes," Purdy, p. 61, Vol. IV, *Trans. A. C. S.*

"Bristol Glazes," Purdy, p. 136, Vol. V, *Trans. A. C. S.*

"Salt Glazes," Barringer, p. 105, Vol. V, *Trans.* A. C. S.

"Enameled Bricks," Barringer, p. 256, Vol. V, *Trans. A. C. S.*

"Stoneware Glazes," Geijsbeek, p. 207, Vol. VI. *Trans. A. C. S.*

"Matt Glazes at High Temp," Binns, p. 115, Vol. VII, *Trans. A. C. S.*

"Bodies and Glazes," Weelans, p. 483, Vol. IX, *Trans. A. C. S.*

"Terra Cotta Glazes," Parmelee, p. 577, Vol. IX, *Trans. A. C. S.*

"Engobes and Glazes," Searle, *Brick*, 1909 (January to May).

"A Cheap Enamel for Stoneware," Stull, p. 618, Vol. XI, *Trans. A. C. S.*

Purpose of Experiment.

The purposes of the following experiment are:

1. To determine the influence of variation in constitution of these varieties of glazes and to develop a relationship between the porcelain and bristol glazes.

2. To determine their fitness for the several purposes.

(*a*) On a porcelain body of the following constitution and biscuited at Cone 4:

5 English ball clay No. 12.
5 Tennessee ball clay No. 9.
10 English china clay.
10 Georgia china clay.
10 Florida china clay.
20 Golding flint.
20 Eureka french flint.
20 Brandywine feldspar.

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(*b*) Robinson Clay Products Co. stoneware clay prepared by stiff mud process in the Mueller auger machine and dried to "Bone dryness."

Outline of Experiment.

The experimental series were divided into five groups, the division being based on the molecular ratio of the RO to the R_2O as follows:

Division into Groups.

	Groups				
	I	II	III	IV	V
$\frac{RO}{R_2O}$	$\frac{8}{2}$	$\frac{6}{2}$	$\frac{4}{2}$	$\frac{3}{2}$	$\frac{2}{2}$

The groups were divided into five series each, the division being based on the molecular ratio of CaO to ZnO as follows:

Division into Series.

	Series				
	A	B	C	D	E
$\frac{CaO}{ZnO}$	$\frac{1}{0}$	$\frac{3}{1}$	$\frac{1}{1}$	$\frac{1}{3}$	$\frac{0}{1}$

Division into Members.

	Members				
	1	2	3	4	5
Eqv. Al_2O_3.....	0.5	0.55	0.6	0.7	0.8

Silica content in equivalents is in ratio with the equivalents of Al_2O_3 as 6 : 1. This is low for porcelain glazes but nearly correct for Bristol. Further work is under way to determine the influence of the increased SiO_2 content.

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TABLE SHOWING MOLECULAR PROPORTIONS FOR EACH GROUP.

Group I.

(25 glazes.)

Division into series				Division of series into members.		
Series No.	Equivalent of			Member No.	Equivalent of	
	CaO	KNaO	ZnO		Al_2O_3	SiO_2
A.....	0.8	0.2	...	1	0.50	3.0
B.....	0.6	0.2	0.2	2	0.55	3.3
C.....	0.4	0.2	0.4	3	0.60	3.6
D.....	0.2	0.2	0.6	4	0.70	4.2
E.....	0.0	0.2	0.8	5	0.80	4.8

Group II.

(25 glazes.)

Division into series				Division of series into members		
Series No.	Equivalent of			Member No.	Equivalent of	
	CaO	KNaO	ZnO		Al_2O_3	SiO_2
A.....	0.75	0.25	.....	1	0.50	3.0
B.....	0.563	0.25	0.1871	2	0.55	3.3
C.....	0.375	0.25	0.375	3	0.60	3.6
D.....	0.187	0.25	0.563	4	0.70	4.2
E.....	.....	0.25	0.75	5	0.80	4.8

Group III.

(25 glazes.)

Division into series				Division of series into members		
Series No.	Equivalent of			Member No.	Equivalent of	
	CaO	KNaO	ZnO		Al_2O_3	SiO_2
A.....	0.666	0.333	.....	1	0.50	3.0
B.....	0.5	0.333	0.167	2	0.55	3.3
C.....	0.333	0.333	0.333	3	0.60	3.6
D.....	0.167	0.333	0.50	4	0.70	4.2
E.....	.....	0.333	0.666	5	0.80	4.8

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Group IV.

(25 glazes.)

Division into series				Division of series into members		
Series No.	Equivalent of			Member No.	Equivalent of	
	CaO	KNaO	ZnO		Al_2O_3	SiO_2
A.....	0.6	0.40	....	1	0.50	3.0
B.....	0.45	0.40	0.15	2	0.55	3.3
C.....	0.3	0.40	0.30	3	0.60	3.6
D.....	0.15	0.40	0.45	4	0.70	4.2
E.....	....	0.40	0.60	5	0.80	4.8

Group V.

(25 glazes.)

Division into series				Division of series into members		
Series No.	Equivalent No.			Member No.	Equivalent of	
	CaO	KNaO	ZnO		Al_2O_3	SiO_2
A.....	0.50	0.50	.....	1	0.50	3.0
B.....	0.375	0.50	0.125	2	0.55	3.3
C.....	0.25	0.50	0.25	3	0.60	3.6
D.....	0.125	0.50	0.375	4	0.70	4.2
E.....	.....	0.50	0.50	5	0.80	4.8

Calculations.

As example of manner of calculating these glazes, that for Member 3 of Series C, Group IV, is here given.

0.3 equiv. whiting = 0.3 × 100	30.0
0.4 equiv. feldspar = 0.4 × 556	222.4
0.3 equiv. zinc oxide = 0.3 × 81	24.3
0.3 equiv. clay = 0.2 × 258	51.6
0.8 equiv. flint = 0.8 × 60	48.0
	376.3

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Procedure.

Materials Used.—The materials used in these glazes were:

Brandywine feldspar.
Mayfield ball clay.
Ohio silica flint.
Whiting.
Zinc oxide.

No soluble salt was added to check crawling.

Making of Glazes.—Each glaze was weighed separately (*i. e.*, not made by blending), the weights in each case being checked by at least two operators.

The glazes were ground for 30 minutes in a 4-gallon ball mill screened and applied by dipping.

Burning.—Since most of these glazes are more nearly of the porcelain than of the Bristol type, it was thought best to try them at heat ranges from cone 6 to cone 12 inclusive. Therefore, the effect of intensity of heat treatment was studied by burning to cones 6, 8, 10 and 12 respectively.

The length of burns varied from 26 to 52 hours, good distribution of heat being obtained in all but the cone 10 burn.

RESULTS OBTAINED.

Cone 7[1] (25 hours) Stoneware Body.

Group I.

Maturity.—

1. Maximum maturity obtained in this group was in Series C. All members of this series have fair gloss, the gloss being unaffected by increase of clay. Members 1 and 2 of Series D likewise have fair gloss.

[1] Three burns were made to obtain one at cone 6 that would be cone 6 throughout the kiln. In the third burn the heat treatment was uniform throughout, but instead of cone 6 we obtained cone 7. In this burn we had the same cone down on the inside of the saggars as on the outside.

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2. The gloss of the remaining members of this group is very slight and such as there is decreases with increase clay content.

3. The gloss remaining equally fair throughout Series C points to the possible conclusion that with CaO and ZnO in the ratio of 1 : 1 increase in clay (from 0.3–0.6 equivalent) will not materially decrease the gloss.

Opacity.—

1. Opacity increases with increase of clay content in all of the series of Group I.

2. Opacity is increased as the zinc is increased at the expense of the CaO.

3. Increase of ZnO is much more effective in increasing opacity than clay.

4. All members of Series C have fair opacity, Members 4 and 5 being as white as tin enamels.

Surface Defects.—

1. Ignoring defects which were obviously due to accidental causes, we find in Series D and E that high clay has caused a separation of the glaze quite similar to cracqueling.

2. No crawling is evident.

Group II, Cone 7.

Maturity.—

1. The members of the series of this group are slightly more glossy than the corresponding members of Group I.

2. Members of Series C again have the best gloss.

3. Increase of clay causes reduction in gloss in all series of this group.

Opacity.—

1. Same as that of Group I.

Group III, Cone 7.

Maturity.—

1. The glazes of this group as a whole are more glossy than those of Group II.

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2. Effect of clay in decreasing gloss is seen in this group also, but not so pronounced in Series D and E (*i. e.*, with high ZnO).

Opacity.—

1. The opacity of Series C of this group is only slightly, if any, less than that of Series C, Group I, notwithstanding the lower content of ZnO (0.333 as compared with 0.4) and greater degree of maturity.

2. Series D and E are white enamels throughout.

3. The members of Series C show gradations in opacity from Member 1 which is a good glossy stoneware white, to Member 5 which has the whiteness of tin enamel although lacking somewhat in gloss.

Surface Defects.—

1. Members of Series D and E are badly cracqueled, those of Series E being the worse. This cracqueling thus seems to be made worse by the increase of ZnO at the expense of CaO.

Groups IV and V, Cone 7.

Maturity.—

1. Except for Series A and B (high CaO) the glazes of these groups have no better gloss than those of Group III, the gloss of Series E being at its best in Group III.

2. In Series A and B the gloss increases continuously from Group I to Group V, but in all other series maximum gloss is attained in Group III (0.333 equivalent feldspar).

Opacity.—

1. Opacity increases with both increase in clay and ZnO as in the preceding groups, the opacity of the members of Series D and E being equal to that of tin enamels.

2. The opacity of Series C decreases slightly from Group III to IV.

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Surface Defects.—

1. With high calcium, the glazes of Group V (Series A) seem to have shrunk, leaving an unglazed margin around the edge of the tile. Those members lowest in clay seem to have shrunk the worst.

2. Crazing is bad in all members of Series A, B and C and in D1 of both Group IV and Group V and in D2 of Group V.

3. Crazing decreases with increase of Al_2O_3 and ZnO.

General Conclusions on Cone 7 Burn.

1. **Good Glazes.**—The only glazes which may be classified as good from a commercial standpoint are the white enamels of Series C (1, 2, 3) and D (1–5 inclusive) of Group III. Member 1 of Series C, Group III is as opaque as the best of Bristol glazes while the other members of this group are much more opaque, and those of Series D, Group III are excellent white enamels.

2. **Influence of Clay.**—(*a*) In the high calcium series, addition of clay increases the refractoriness.

(*b*) When ZnO is 0.4 equivalent or more, increase of clay appears to have but slight effect on the gloss of the glaze. This is more pronounced as the feldspar increases, due perhaps to the total clay content, being less and less as the feldspar increases.

(*c*) Increase of clay in any of the series causes increase in opacity.

(*d*) In these studies, increase of clay has not caused increased cracqueling nor increased shrinkage of the glaze.

3. **ZnO versus CaO.**

(*a*) Members 1 containing no ZnO and 0.50 equivalent Al_2O_3 are transparent.

(*b*) As the ZnO increases the glazes become more opaque, good opacity not being obtained with less than 0.333 ZnO unless the Al_2O_3 content exceeds 0.55 equivalent.

(*c*) Crazing decreases with increase of ZnO.

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(*d*) With low feldspar (less than 0.4 equivalent) maximum gloss is obtained when the ratio of CaO to ZnO is less than 1:1 while with higher feldspar the ratio of calcium to zinc must be higher, *i. e.*, at least 3:1.

4. **Effect of Feldspar.**

(*a*) With the lowest Al_2O_3 content here experimented with (0.5 equivalent), maximum gloss is attained with 0.333 equivalent of feldspar.

(*b*) Feldspar increases tendency to craze.

(*c*) The crazed glazes are:

Group III, Series A, Members 1, 2 and 3.
Group III, Series B, Members 1 and 2.
Group IV, Series A, Members 1–5 inclusive.
Group IV, Series B, Members 1, 2 and 3.
Group IV, Series C, Members 1, 2 and 3.
Group IV, Series D, Members 1 and 2.
Group V, Series A, Members 1–5 inclusive.
Group V, Series B, Members 1–5 inclusive.
Group V, Series C, Members 1–4 inclusive.
Group V, Series D, Members 1 and 2.

(*d*) To counteract crazing, decrease the feldspar and increase the zinc and clay.

(*e*) Except in Series A and B, mere increase of K_2O (at the expense of CaO and ZnO) does not affect opacity, and with this it follows that since the total amount of clay used as a source of Al_2O_3 decreases as the feldspar increases, any statement which has been made to the effect that increase of clay increased opacity must be considered as applying only to the results obtained in a given series where the equivalent of feldspar, zinc oxide and whiting remains constant.

Cone 8+ (28 hrs.) Stoneware.

Comparison with Cone 7 Burn.

1. Except for increased gloss the glazes with this heat treatment show the same evidence noted in the cone 7 burn.

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2. Maximum gloss is obtained in Group IV (feldspar 0.4 equivalent).

3. The gloss of Group II with this heat treatment is the same as that attained in Group VII at cone 7.

Good Glazes.—The glazes which, except for crawling (see p. 18), would be fair or good stoneware glazes, with this heat treatment (cone 8) are, for Group I–III inclusive, as follows:

Series	Members				
A	1	2	3	.	.
B	1	2	3	4	.
C	1	2	3	4	5
D	1	2	3	4	.
E	.	.	.	.	.

In Group IV all of Series C and Members 1, 2, 3 and 4 of Series D would be good stoneware glazes. When clay exceeds 0.1 equivalent, however, care would have to be exercised to prevent the glaze from parting in drying for when the glaze surface is thus broken, crawling of the glazes containing ZnO invariably follows.

Nearly all the glazes of Group V and those of Series A and B of Group IV are crazed.

Opacity.—None of the glazes are perfectly transparent, Members 1 and 2 of Series A being the most so.

The glazes are not any less opaque with this heat treatment than they were at cone 7. For a cheap enamel with this heat treatment (and they were good at cone 7) attention is called to Members 1, 2 and 3 of Series C, Group III in which the zinc oxide content varies from 8.2 to 7.13 per cent. as compared to the 10 per cent. and more content in a great many Bristol glazes used in factories to-day. See Stull, p. 610, Vol. XI, *Trans. A. C. S.*

Increase of feldspar has not decreased the opacity, *i. e.*, with a given Al_2O_3 content and a given ratio of CaO to ZnO, we have equivalent opacity without regard to the source of the Al_2O_3, *i. e.*, whether from feldspar or clay.

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Crawling.—Owing to some cause (not fully known) some of the glazes crawled badly. The only known factor that would have influence in promoting crawling in this investigation was the fact that heavy wads were used between the saggars and the heat was brought up rapidly, thus possibly causing the generation of steam within the saggars. Crawling has occurred at hit and miss places through the groups and series thus giving no evidence as to influence of change in constitution of the glaze.

In this cone 8 burn, there was no parting of the glaze similar to cracqueling.

Crazing.—Crazing is seen in:

Group IV, Series A, Members 1 and 2.
Group IV, Series B, Members 1.
Group V, Nearly entire group.

Cone 8 Porcelains

Good Glazes.—

Group I,	Series A,	Member 1, 2
Group I,	Series B,	Member 1, 2, 3
Group I,	Series C,	Member 1, 2, 3, 4
Group I,	Series D,	Member 1, 2, 3, 4
Group II,	Series A,	Member 1, 2, 3
Group II,	Series B,	Member 1, 2, 3, 4
Group II,	Series C,	Member 1, 2, 3, 4, 5
Group III,	Series D,	Member 1, 2, 3, 4
Group III,	Series A,	Member 1, 2, 3, 4
Group III,	Series B,	Member 1, 2, 3, 4, 5
Group III,	Series C,	Member 1^1, 2^1, 3^1, 4^1, 5^1
Group III,	Series D,	Member 1^1, 2^1, 3^1, 4^1
Group IV,	Series A,	Member 1, 2, 3, 4, 5
Group IV,	Series B,	Member 1, 2, 3, 4, 5
Group IV,	Series C,	Member 1^1, 2^1, 3^1, 4^1, 5
Group IV,	Series D,	Member 1^1, 2^1, 3^1, 4^1

The glazes of Group V either crazed or have too much of an egg-shell texture.

[1] Glazes marked with [1] are the best.

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Cone 10 + (49 hours) Stoneware and Porcelain

In this burn the distribution of heat was not as good as desired, and the conditions attending the firing prolonged the burn to an undesired length of time, resulting in a much inferior burn to the two just studied.

Inasmuch, however, as these same series of glazes were studied last year, we have a good check on the cone 10 heat treatment. The following notes, therefore, are composits of the results obtained on these two occasions.

In general the results obtained check those of the preceding burn (cone 8).

The degree of opacity on the stoneware body has not been impaired to any noteworthy degree by the increase in heat treatment, nor has the prolonged heating seemed to have had material effect, except in glazes which have the maximum zinc content, *i. e.*, in Series D, Groups I, II and III. In these, the glazes are less glossy.

The best glazes are found in Group III and IV, Series C and D.

The gloss on the porcelain body while quite pronounced is not as good on the average of all trials as in the cone 8 burn. Those of the cone 8 were smooth glasses, while those of this burn are more on the egg-shell order.

Cone 12 (52 hours) Stoneware

The effect on opacity of increased heat treatment from cone 10 to 12 can not be discussed wholly from the trials at hand because in the cone 12 we had some flashing that brought the iron spots from the body through the glaze. In the experiments made on this same series of glazes last year, the gloss in the low zinc glazes was not impaired by the increased heat treatment but the opacity of the high zinc was reduced. The results this year apparently check those of last year in that the gloss of glazes in Series A of each group is brighter, if anything, than that of the gloss of same glazes in the cone 10 burn.

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The gloss of Series E of Group I to III, inclusive, is completely lost while that of Series E, Group V is not decreased to any extent with this heat treatment.

Good gloss is obtained in Series A, B, C of Group I, II and III, and in Series A, B, C, D of Group IV, and in all the Series of Group V.

With this heat treatment, the effect of clay is about the same as in the preceding burns except that when feldspar is less than 0.5 equivalent (Group V), the members of Series D and E (high zinc) have suffered a decided loss in gloss, this loss being the greatest in Group I and progressively less as the feldspar increases.

Crazing with this heat treatment is just the same as with the less severe heat treatment.

Cone 12 (Porcelain)

1. The good glazes with this heat treatment are as follows:

Group	I, Series A,	Members 1, 2, 3
Group	I, Series B,	Members 1, 2, 3, 4, 5
Group	I, Series C,	Members 1, 2, 3
Group	I, Series D,	Members 1, 2, 3
Group	II, Series A,	Members 1, 2, 3
Group	II, Series B,	Members 1, 2, 3, 4, 5
Group	II, Series C,	Members 1^1, 2^1, 3^1, 4^1, 5^1
Group	II, Series D,	Members 1^1, 2^1, 3^1, 4^1
Group	III, Series A,	Members 1, 2, 3, 4
Group	III, Series B,	Members 1, 2, 3, 4
Group	III, Series C,	Members 1^1, 2^1, 3^1, 4^1, 5
Group	III, Series D,	Members 1, 2, 3, 4, 5
Group	IV, Series A,	Members 1, 2, 3, 4, 5
Group	IV, Series B,	Members 1, 2, 3, 4, 5
Group	IV, Series C,	Members 1, 2, 3, 4, 5
Group	IV, Series D,	Members 1, 2, 3, 4, 5
Group	IV, Series E,	Members 1, 2, 3
Group	V, Series A,	Members 4, 5 crazed

[1] Glazes marked with [1] are the best.

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Group V, Series B, Members 3, 4, 5
Group V, Series C, Members 2, 3, 4, 5
Group V, Series D, Members 2, 3, 4, 5
Group V, Series E, Members 1, 2, 3, 4

2. The best glazes of the entire burn on porcelain are in Group III, Series C.

3. As the feldspar increases, the Al_2O_3 content may be present in larger amounts without impairing the gloss or texture.

With the maximum feldspar, high Al_2O_3 is required to overcome the finely rippled surfaces peculiar to egg shells. These egg shell surfaces are greatly like the surface produced by overfiring softer glazes, and since we find this egg shell finish increasing with increasing heat treatment, it may be also said to be due in this instance to overfiring, but we find this peculiar texture more characteristic of the high feldspar glazes which we know are not as fusible as the glazes of Groups III and IV.

Except in Groups IV and V, the glazes highest in zinc (Series E) are dull and dry.

Summary

In the following charts will be found letters denoting comparative gloss, opacity and crazing. The symbols used are:

Dr represents dry.

Du represents dull.

SG—, SG, SG+, G—, G, represent successive degrees of glossiness from a slight sheen to good bright glossy surface.

T, T—, SO—, SO, SO+, O—, O, O+ represent successive degrees of opaqueness ranging from transparency to a very good white enamel.

C represents crazing.

Opaque Glossy Glazes.—The rectangular spaces marked off by dotted lines are the areas of best opaque glossy glazes at each of the heat treatments.

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CONE 7 STONEWARE

	Groups	I	II	III	IV	V
A.....	1	SG, T	SG, T	G—, T	G—, T, C	G, T, C
	2	SG, T	SG—, T	G—, T	SG, T, C	SG, T, C
	3	SG—, T	SG—, T	SG—, T	Du, C	SG—, T, C
	4	Du	Du	Du	Du, C	Du C
	5	Dr	Dr	Dr	Du, C	Du, C
B.....	1	SG, T	SG+, T	SG+, T—	G—, T—, C	G—, T, C
	2	SG, T	SG, T	SG+, T—	SG+, T—, C	G—, T, C
	3	SG—, T	SG—, T	SG, T—	SG—, T—, C	SG+, T, C
	4	Du	SG—, SO—	Du	SG	SG, C
	5	Dr	Dr	Du	SC—	SG, C
C.....	1	G—, SO—	SG+, SO	G, SO—	G, SO—, C	G—, SO—, C
	2	G—, SO—	SG+, SO	G, SO—	G—, SO—, C	SG+, SO, C
	3	G—, SO—	SG+, O	G, SO	G—, SO, C	SG+, SO, C
	4	G—, O	SG, O	SG, O	SG—, O	SG—, O—, C
	5	G—, O+	SG, O	SG, O	SG, O	SG, O
D.....	1	SG, O+	SG, O+	G, O	G, O, C	SG+, O+, C
	2	SG, O+	SG, O+	G, O+	G—, O+	SG—, O+, C
	3	SG, O+	SG, O+	G, O+	G—, O+	SG+, O+
	4	SG—, O+	SG, O+	G, O+	SG+, O+	SG, O+
	5	Du, O	Du, O+	G, O+	SG, O+	SG, O+
E.....	1	Du	Du	G, O+	SG, O+	Du, O
	2	Du	Du	G, O+	SG, O+	Du, O
	3	Du	Du	G, O+	SG, O+	SG—, O+
	4	Du	Du	G, O+	SG, O+	SG—, O+
	5	Dr	Dr	G, O+	SG, O+	SG, O+

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CONE 8 STONEWARE

Groups		I	II	III	IV	V
A.	1	SG, T	SG+, T	SG+, T	G—, T, C	G—, T, C
	2	SG, T	SG, T	SG+, T	G—, T, C	SG+, T, C
	3	SG, T	SG, T	SG+, T	G—, SO—	SG+, SO—, C
	4	Du	SG—	SG, T	SG, SO—	SG+, SO—, C
	5	Du	Du	Du, SO—	SG—, SO—	G—, SO—
B.	1	SG, T	SG+, T	G—, SO+	SG+, SO—, C	SG+, T, C
	2	SG, T	G—, T	G—, O—	SG+, SO—	SG+, SO—
	3	SG, SO—	G—, SO—	G—, O—	SG+, SO—	SG+, SO—
	4	SG, SO—	SG, SO—	G—, O	SG+, SO	SG+, SO—
	5	SG—, SO—	SG, O	SG, O	SG, SO—	SG, SO—
C	1	G—, O	G, SO	G, O	G, SO—	G, SO—, C
	2	G—, O	G, O	G, O	G, SO—	G, SO
	3	G—, O	G, O	G, O	G, SO—	G, SO
	4	G—, O	G, O	G, O	G, SO	G, O—
	5	G—, O	G, O	G—, O	G, SO	G, O
D.	1	G—, O	G, O	G, O+	G, O	G—, SO
	2	G—, O	G, O	G, O+	G, O	G—, O—
	3	G—, O	G, O	G, O+	G, O	G—, O
	4	G—, O	G, O	G, O+	G, O+	SG+, O
	5	SG+, O	G, O	G—, O+	G, O+	SG+, G
E.	1	SG+	G—, O+	G—, O+	SG+, O+	SG+, O+
	2	SG	G—, O+	G—, O+	SG+, O+	SG+, O+
	3	Du	G—, O+	G—, O+	SG+, O+	SG+, O+
	4	Dr	SG+, O+	SG, O+	SG+, O+	SG+, O+
	5	Dr	SG, O	SG	SG, O+	SG+, O+

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CONE 10 STONEWARE

		Groups I	II	III	IV	V
A.....	1	SG, T	SG, T	SG, T	SG+, T	G—, T
	2	SG, T	SG, T	SG, T	SG+, T—	G—, T
	3	SG, T—	SG, T—	SG, T	SG+, T—	G—, T—
	4	SG—, T—	Du, SO—	SG—, SO—	SG, T—	SG, T—
	5	Du	Dr+	Du	SG—, SO—	SG, SO—
B.....	1	SG, T—	SG+, T	.....	G—, T	G—, T
	2	SG+, T—	G—, T	.....	G—, T	G—, T
	3	SG, T—	G—, T—	SO—	G—, T—	G—, SO
	4	SG, SO—	G—, SO—	G—, SO—	G—, SO—	G—, SO
	5	SG—	SG+, SO	SG, SO—	SG+, SO—	SG, SO
C.....	1	G—, SO	G, SO—	G, SO	G, T—	G, T
	2	G—, SO	G, SO—	G, SO	G, T—	G, T—
	3	G—, SO	G, SO	.....	G, T—	G, T—
	4	G—, SO	G, SO+	G, SO+	G, SO	G, SO
	5	SG+	G—, O	SG+, SO+	G, O—	G—, SO+
D.....	1	G, O	G, SO—	G, O	G, O—	G, SO
	2	G, O+	G, SO	G, O	G, O	G, SO+
	3	G—, O+	G—, O	G, O+	.....	G—, SO+
	4	G—, O+	SG+, O	G, O+	G, O+	G—, O
	5	G—, O+	SG+, O	G—, O	G, O+	G—, O
E.....	1	SG—, O+	G—, O	G—, O	G—, O	G—, O
	2	SG+, O+	G—, O	G—, O+	.....	G+, O+
	3	SG,	G—, O+	G—, O+	.....	G, O+
	4	.....	SG+, O+	SG+, O	G—, O+	G, O+
	5	Dr	SG+, O+	SG	SG+, O	G, O+

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CONE 12 STONEWARE

Groups		I	II	III	IV	V
A.....	1	SG+, T—, C	SG+, T—	SG, T—, C	SG, SO, C	SG+, T, C
	2	SG+, T—, C	SG, T—	SG, T—	SG, SO, C	SG+, T, C
	3	SG, SO, C	SG, SO—	SG, T—	SG, SO, C	SG+, T, C
	4	SG, SO, C	SG, SO—	SG, SO—	SG, SO	SG, T, C
	5	SG—, SO, C	SG, SO—	SG, SO	SG, SO, C	SG, SO—, C
B.....	1	SG+, SO—, C	SG+, T—	SG+, SO—	SG+, SO, C	SG+, T, C
	2	SG+, SO—, C	SG+, T—	SG+, SO—	SG+, SO, C	SG+, T, C
	3	SG+, SO—	SG+, SO—	SG+, SO	SG+, SO, C	SG+, T, C
	4	SG+, SO	SG+, SO—	SG+, SO	SG+, SO+, C	SG+, T—, C
	5	SG, SO—	SG+, SO	SG+, SO+	SG+, SO+	SG+, SO—, C
C.....	1	G, SO	G, SO	G, SO+	G—, SO—	G—, T—, C
	2	G, SO	G, SO	G, SO+	G—, SO—	G—, SO—, C
	3	G, SO	G, SO	G, SO+	G—, SO—	G—, SO,—C
	4	G, SO	G, SO	G, SO+	G—, SO	G—, SO, C
	5	G—, SO	G—, SO	SG, SO+	SG+, SO	G—, SO+, C
D.....	1	G, SO	G, O	G, SO	G, O	G—, C
	2	G, O	G, O	G, SO	G, O	G—, C
	3	G—, O	G, O	G, O	G, O	SG+, C
	4	G—, O	G, O	G, O	G, O	SG, C
	5	SG, O	SG, O	SG, O	G—, O	SG, C
E.....	1	SG	SG	Du	G—	G, C
	2	Du	Du	Du	G—	G, C
	3	Du	Du	Du	G—	G—, C
	4	Dr	Du	Du	SG+	SG+, C
	5	Dr	Dr	Dr	SG	SG+, C

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The percentage composition of the extreme glaze of each series included within the largest of these rectangles are here given:

Glaze	C_1			C_5		
Groups	II	III	IV	II	III	IV
Whiting	11.4	10.1	9.2	7.8	6.9	6.3
Feldspar	41.9	56.3	68.2	28.9	53.7	46.7
Clay	19.4	13.1	7.9	29.5	25.2	21.7
Flint	18.1	12.2	7.4	27.4	23.5	20.2
Zinc oxide	9.2	8.2	7.5	6.3	5.6	5.1
Total	100.0	99.9	100.2	99.9	99.9	100.0

Glaze	D_1			D_5		
Groups	II	III	IV	II	III	IV
Whiting	5.6	5.1	4.6	3.9	3.5	3.2
Feldspar	42.8	57.0	69.0	29.1	39.0	47.1
Clay	19.7	13.2	8.0	29.8	25.4	21.8
Flint	18.3	12.3	7.4	27.6	23.6	20.2
Zinc oxide	13.8	12.5	11.2	9.6	8.5	7.7
Total	99.9	100.1	100.2	100.0	100.0	100.0

The composition of the intermediate glazes could be obtained by interpolation from those given above.

Of these glazes, those of Group III and Group IV are in all respects the best. Group IV, D2 is practically the same glaze as glaze VI, D recommended by Purdy in Vol. V, *Transactions A. C. S.*, p. 165, as being a good opaque glaze maturing well at cone 6. In this experiment it has excellent heat range (7–12) and has very fair opacity. Molecular formula for IV, D2 is:

$$\left.\begin{matrix} 0.40\ K_2O \\ 0.15\ CaO \\ 0.45\ ZnO \end{matrix}\right\} 0.55\ Al_2O_3\ 3.3\ SiO_2$$

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Glaze V, D2 is quite similar to Parmelee's H-30 (p. 595, Vol. IX, *Trans. A. C. S.*) and to the one recommended by Purdy in his first paper (p. 76, Vol. IV, *Trans. A. C. S.*). While this glaze has excellent heat range, opacity, etc., on flat tile, our general experience with the glazes in Group V, which contains 0.5 equivalent feldspar, gives emphasis to the warning given by Purdy that on wares burned under commercial conditions, this glaze would not be as free from physical defects as would those containing less feldspar. Factory experience by former students of the Ohio State University, Ceramic Department, in every instance checks Purdy's findings in this respect.

Opacity

Our summary on opacity will be made in the following order:

A. Influence of *ZnO*
B. Influence of *CaO*
C. Influence of *ZnO* vs. *CaO*
D. Influence of Al_2O_3
E. Influence of *Clay*
F. Influence of *Feldspar*
G. Influence of *Heat treatment*

A. *Influence of ZnO.*

1. Since, on comparing corresponding members of the series in any group, we find that the opaqueness of the glaze increases rapidly with each increment of ZnO, it follows that ZnO operates decidedly in producing opacity.

2. As low as *0.375 ZnO with 0.5* Al_2O_3 (V, D1) and *0.15 ZnO with* 0.8 Al_2O_3 (IV, B5) produces opacity equal to the best used on stoneware. This is in accordance with Purdy ("Bristol Glazes," Vol. IV, *Trans. A. C. S.*) who gives as his lower limit of ZnO content with 0.5 Al_2O_3 as 0.35 equivalent. None of his glazes, however, contained more than 0.5 Al_2O_3, which accounts for the fact that his lower limit of ZnO content is higher than that found in this investigation.

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B. *Influence of CaO.*

1. In passing from group to group, the opacity of corresponding members and series remains practically the same in spite of the fact that ZnO and CaO are decreasing simultaneously. This may result from the decreased CaO, causing either a decrease in the amount of molten solvent, leaving more of the glaze ingredients as undissolved or suspended matter, or in a decrease in the solvent action of the molten flux. Then again, since we know that in mixtures of calcium oxide and clay we have decided chemical reactions resulting in a complete recast of the constitution of the mixture, the composition of the new compounds thus formed being of at least three sorts,[1] we might argue that this constancy in opacity in the corresponding members from group to group may be due in part to the formation of certain $CaO-Al_2O_3-SiO_2$ compounds as suggested by Parmelee.[2] We believe, however, that aside from the change in the amount or in the solvent action of the molten flux, or in the possibility of the separating out of new $CaO-Al_2O_3-SiO_2$ compounds, this constancy in opacity in the corresponding members from group to group may be due (at least in part) to the mere increase of feldspar.

In the following table is given the percentage composition of the extremes of Series C in each of the five groups. The opacity of each of these extremes, as well as that of the intermediates of this series, did not differ from group to group. This same constancy in opacity of the corresponding series and members from group to group was exhibited in all the series.

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[1] Rieke, Sprechsaal, No. 45, 1907.
[2] Trans. A. C. S., Vol. IX.

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Material	Member 1, Series C — Group I	II	III	IV	V
Whiting	12.0	11.4	10.1	9.2	7.7
Feldspar	33.4	41.0	56.3	68.2	86.1
Clay	23.2	19.4	13.1	7.9	.....
Flint	21.6	18.1	12.2	7.4	.....
Zinc oxide	9.7	9.2	8.2	7.5	6.3
Total	99.9	100.0	99.9	100.2	100.1

Material	Member 5, Series C — Groups I	II	III	IV	V
Whiting	8.3	7.8	7.0	6.3	5.3
Feldspar	23.0	28.9	38.7	46.7	58.7
Clay	32.1	29.5	25.2	21.7	16.4
Flint	30.0	27.4	23.4	20.2	15.2
Zinc oxide	6.7	6.3	5.6	5.1	4.3
Total	100.1	99.9	99.9	100.0	99.9

C. *Influence of ZnO vs. CaO.*

From Series C, where the ratio of CaO : ZnO is as 1 : 1, to Series E containing no CaO the opacity is decidedly increased, and from Series C to Series A (containing no ZnO) the opacity is decidedly decreased. This shows that ZnO is positively an opacifier while CaO certainly adds nothing to the opaqueness of the glazes even when present in amount as high as 0.8 equivalent (Gr. 1, Series A). This is contradictory to the impression received from a statement by Parmelee, p. 597, Vol. I X, *Trans. A. C. S.*

D. *Influence of Al_2O_3.*

1. By comparing Members 1 to 5 in Series A (which contains no ZnO)we find that the degree of opaqueness is

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the same for corresponding members in each of the groups, notwithstanding the fact that as we pass from Group I to V, the equivalent of K_2O is increasing at the expense of CaO and the Al_2O_3 is being derived more and more from feldspar, and the content of free flint is progressively decreasing.

2. As pointed out under the heading "Influence of ZnO," 0.15 equivalent of ZnO requires 0.8 equivalent Al_2O_3 to produce opacity equal to that produced with 0.375 equivalent ZnO and 0.5 equivalent Al_2O_3. Since these glazes are highly viscous, and as glasses are far from perfect solutions, and since increased opaqueness in these glazes is nearly always due to material in suspension which has either never been in solution or has crystallized out from solution, and again, since CaO has been found empirically to react more readily and in larger proportions with clay than does ZnO, it is not difficult to figure that with high CaO we must have more clay to obtain equi-opacity.

Rieke (*Sprechsaal*, No. 46, 1907) found $3CaO,Al_2O_3$, $4\ SiO_2$ to be the most fusible mixture of these oxides. Since in such fusions it has been found that, of the calcium aluminum silicates, anorthite is the most readily formed, we can assume that Rieke's mixture was:

$$CaOAl_2O_32SiO_2 + 2CaOSiO_2.$$

Now since Vogt found that orthoclase and anorthite formed a slight eutectic when mixed in equal proportions, we have as a most fusible mixture something of the following:

$K_2OAl_2O_36SiO_2$(orthoclase)
$CaOAl_2O_32SiO_2$(anorthite)
$2CaO2SiO_2$(wollastonite)

$$\left.\begin{matrix}1.0\ K_2O \\ 3.0\ CaO\end{matrix}\right\} 2\ Al_2O_3\ 10.0\ SiO_2$$

Reducing this to 1 RO we have

$$\left.\begin{matrix}0.25\ K_2O \\ 0.75\ CaO\end{matrix}\right\} 0.5\ Al_2O_3\ 2.5\ SiO_2,$$

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which practically corresponds with our glaze, II, A1, and with the mixture which Seger (p. 236, Vol. I) found to be the most fusible with this SiO_2 content (3.5). Since there is a eutectic between wollastonite and flint, and feldspar and flint, it is not surprising that Seger found it necessary to increase the SiO_2 from 2.5 to 4.0 in order to obtain greater fusibility (see cone 4).

Now, if we add clay to the above mixture together with the free SiO_2 necessary to retain the Al_2O_3–SiO_2 ratio of 1 : 6, there would not be any substance with which the clay could react chemically at these temperatures; hence, clay would have to remain suspended in the molten matrix as undissolved material and as such would add to the opacity. Zinc added to this mixture in increasing amounts would at first cause easier fusion, and then progressively greater opacity. In case of corresponding members of each of the series in any one group, we have the CaO–ZnO ratio varying, *i. e.*, as the ZnO increases the CaO decreases; hence, in these experiments we have the progressively increased opacity from series A to E due not only to the ZnO excess but also to the fact that we have less and less CaO to react with the clay, thus leaving more and more of the clay in suspension. Calcium oxide in any of these mixtures, therefore, can not be considered as an opacifier, either directly or indirectly in the manner suggested by Parmelee (p. 597, Vol. IX, *Trans. A. C. S.*).

Comparison of the effect of CaO and ZnO in simple mixtures is obtained in V, A1 and V, E1. In V, A1 we have 0.5 equivalent feldspar and 0.5 equivalent whiting and in V, E1 we have 0.5 equivalent feldspar and 0.5 equivalent zinc.

Recalculating V, A1 into the mineral components which our best authorities say we would obtain, we find:

0.25 equiv. leucite ($K_2OAl_2O_34SiO_2$)
0.25 equiv. orthoclase ($K_2OAl_2O_36SiO_2$)
0.50 equiv. wollastonite ($CaOSiO_2$)

This mixture at cone 7 is a good transparent glass

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badly crazed and so shrunk as to have left a border of unglazed tile on all the edges. That this mixture should be more fusible than feldspar is readily explained by laws of solutions, and we fail to see how Seger could have found this mixture so refractory (see Seger, p. 232, Vol. I).

Mixture V, E, on the other hand, covers the tile completely as a thin sheet of white enamel. It has considerable gloss but its surface is pitted as though it had been affected by sulphur.

The zinc-feldspar mixture certainly is more fusible than feldspar alone, but at cone 7 it is far from being a homogeneous glass.

At cone 10, V, A1 has so attacked the body as to give the appearance of a thin, perfectly clear glaze over a gray underslip, whereas at this same cone, V, E1 is a good white enamel, having a few craze marks as its only blemish.

E. *Influence of Clay.*

1. Replacement of Al_2O_3 from clay by Al_2O_3 from feldspar has no effect on opacity.

2. Increase of clay from member to member increases opacity. Reasons for these effects of variation in clay content have been given in the discussions under D.

F. *Influence of Feldspar.*

1. Increase of feldspar from group to group has little or no effect on opacity.

G. *Influence of Heat Treatment.*

1. Increased heat treatment has but slight effect on opacity due, no doubt, to the fact that these glazes do not form perfect solutions in the temperature ranges included in this experiment. Increasing the heat treatment from cone 10 to cone 12 has caused the glazes to dissolve material from the body, producing the effect similar to a light gray underslip beneath a transparent glaze. Glazes which were transparent at the lower cones are still transparent at cone 12. The fact that the upper surfaces of the glazes are not

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made opaque by this dissolved material is due to the extreme viscosity of the glaze. That this lower layer is very light in color even on a fire clay body in a "flash" burn is worthy of study.

HEAT RANGE.

A. *Influence of Change of Ratio of RO to R_2O.*

K_2O *vs.* **CaO** (Series A).—With 0.20–0.25 K_2O the glazes are hard slips except at cone 12. As the K_2O increases from 0.2 to 0.5, the ratio of Al_2O_3 to SiO_2 being constant, the glazes show fluidity at cone 7, with 0.33 K_2O 0.67 CaO although the lack of good gloss of this same glaze at cones 8, 10 and 12 indicates that the progress of fusion is very slow and quiet, there not being sufficient SiO_2 present for perfect solution.

With 0.4 K_2O 0.6 CaO, Members 1 and 2 show, at cone 7, little more evidence of fluidity than those with less K_2O but at cones 8 and 10, these glazes show evidence of boiling, while at cone 12 they are smooth coatings but lack in gloss the same as that which those of the preceding series displayed at cone 12 and approached at cone 10.

With 0.5 K_2O 0.5 CaO, Members 1, 2 and 3 display this boiling tendency from cone 8 to cone 12, although at cone 12 these glazes, where thin, have attained the same degree of glassiness as those lower in K_2O.

The evidence indicates that with less than 0.4 K_2O, the glazes pass from a slip to a glaze with little disturbance to its surface, except in the case of the 0.33 K_2O glazes at cone 7, and that none of the glazes in Series A, Groups I, II and III would be classed as matured unless it be at cone 12, which gives not a glaze but a shiny cintered slip. How far above cone 12 the members of these series could be carried before serious deterioration occurs cannot be determined from the evidence at hand, but it is doubted whether, with this Al_2O_3–SiO_2 ratio, a good bright glaze could be obtained.

The glazes of Series A, Group III, have the longest heat range within which they remain as smooth semi-

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glossy coatings and of the member of Series A, we find the maximum heat range with 0.55 equivalent of Al_2O_3.

K_2O *vs.* ZnO (Series E).—As the K_2O increases in this series at the expense of the ZnO, the first glaze which shows gloss at cone 7 is with 0.33 K_2O 0.67 ZnO. With 0.4 K_2O 0.6 ZnO we find the same evidence of boiling which was displayed in the analogous glazes of Series A.

At cone 8, Member 1 of Series E in Groups I–IV, inclusive, and Member 2, Series E, Group V are good glossy enamels, whereas the other members of this series either lack in gloss or have the pin-hole evidence of having boiled.

At cone 10 the only glazes in Series E which are smooth glossy enamels free from this pin-hole blemish are Members 1 and 2, Group II and III, and Members 3 and 4 of Group V (Members 2 and 3 of Series E, Group IV, are missing).

At cone 12 the glazes of Series E in Groups I–III inclusive (being less than 0.4 K_2O) have suffered so from volatilization of ZnO that they are mere scums. With 0.4 K_2O or more (Group IV and V), glazes of this series have resisted the tendency to volatilize and are good with the exception of Member 5, Group IV, which has 0.8 Al_2O_3 and which shows a tendency to dryness.

The heat range (within which glazes of this RO are good glossy coatings) seems to depend entirely upon the ability of the glaze to hold the zinc from volatilizing. With low feldspar and high clay (Groups I and II, and Members 3 to 5, Groups III and IV and Member 5 of Group V) the glaze cannot prevent volatilization of the ZnO. When the ratio of feldspar to clay is higher, the glazes seem to have formed glasses of sufficiently high viscosity as to prevent volatilization and hence maintain a good glossy surface throughout longer range of heat treatment.

K_2O *vs.* CaO + ZnO.

Cone 7.—The good glazes of this RO combination obtained at cone 7 are those of Series C and D, Group III. With K_2O less than 0.33 equivalent, we find lack of gloss, and with more than 0.333 equivalent K_2O we find that the

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glazes have pitted surfaces and the appearance of having been solidified while boiling.

Cone 8.—The glazes of Series C and D have developed to good glazes in Group I to IV inclusive.

Cone 10.—We have good glazes in Members 1, 2 and 3 of Series C and D in Groups I to IV inclusive, and in Members 1 and 2 of Series D, Group V, and Members 1 and 2 of Series E, Groups II, III and IV.

Cone 12.—None of the glazes can be said to be good at cone 12 because they have not smooth glossy surfaces. In general, when K_2O–CaO and ZnO are present as the RO, we have the longest heat range in Group III and Group IV, Series C and D.

Feldspar vs. Clay.—As feldspar increases from group to group and the clay content proportionally decreased, the Al_2O_3 from clay is being replaced by Al_2O_3 from the feldspar. As the feldspar increases, the glazes change from slips in Group 1 to semi-glazes with glossy surfaces in Groups III and IV. We find the longest heat range within which these mixtures maintain their maximum development as glazes or slips in Group III when the ratio of CaO to ZnO is equal to or more than 1:1 and in Group IV when the ratio of CaO to ZnO is less than 1:1.

Within any group of this study, addition of clay will shorten the heat range.

In a study of similar glazes but containing 0.4 ZnO in all cases, and at least 0.05 equivalent clay, Purdy (Vol. 5, *Trans. A. C. S.*) found that the most fusible glazes were obtained with 0.3–0.4 equivalent of feldspar. These experiments show that this conclusion is true when the ratio of ZnO to CaO is between 1 : 1 and 3 : 1.

EFFECT OF CLAY.

Fusibility.—Comparing the extremes of the series, it is noted that within any group, increase of clay decreases the fusibility of the mixtures. In Groups I and II we probably started (according to Purdy's curves, p. 158, Vol. V,

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Trans. A. C. S.) with the most fusible mixtures and added clay to them, while in the other groups, we started with mixtures which already had been made less fusible by additions of clay, hence we should expect to have increased refractoriness. A *decrease* of clay in Group I from 0.3 equivalent to 0.0 equivalent would no doubt have *likewise decreased* the fusibility of the glazes of this group.

By interpolating for points of 0.5 equivalent Al_2O_3 on Purdy's curves, we find that with this Al_2O_3 content there should be an increase in fusibility from Group I to Group IV and then a decrease to Group V. In Series C and D where we have somewhat the same RO combinations as used by Purdy, we find this same change in fusibility, the glazes of these series being at their best in Groups III and IV. In Series A, however, we find that with equal Al_2O_3 content we apparently have increased fusibility with each increase of feldspar even from Group IV to Group V.

Any additions of clay in Series C and D resulting in a content of Al_2O_3 of more than 0.5 equivalent would decrease the fusibility of the glazes, and so far as can be judged from the tiles, the ratio of this decrease is equal in all groups.

Calculating the probable equivalents of minerals which, from studies in geo-chemistry, we judge would be formed by fusion of the glazes in Series A, we have:

	Group 1		Group 2		Group 3		Group 4		Group 5	
	A1	A5	A1	A5	A1	A5	A1	A5	A1	A5
Orthoclase	0.2	0.2	0.25	0.25	0.333	0.33	0.35	0.4	0.5	0.5
Leucite	...	...	....	....	.....	.....	0.05	...	...	...
Anorthite	0.3	0.6	0.25	0.25	0.167	0.467	0.1	0.4	...	0.3
Wollastonite	0.5	0.2	0.50	0.20	0.50	0.199	0.5	0.3	0.5	0.2
Free SiO_2	0.7	2.2	0.5	2.0	0.18	0.67	0.5	1.4	0.5	1.0

We will not attempt to draw conclusions from these data but offer them as suggestions for study.

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Calculating the molecular ratios of K_2O to Al_2O_3 as was done by Purdy (p. 158, Vol. V, *Trans. A. C. S.*) we find the following:

Member	Groups				
	I	II	III	IV	V
1	1 : 2.5	1 : 2.0	1 : 1.66	1 : 1.25	1 : 1.0
2	1 : 2.75	1 : 2.2	1 : 1.84	1 : 1.4	1 : 1.1
3	1 : 3.0	1 : 2.4	1 : 2.0	1 : 1.5	1 : 1.2
4	1 : 3.5	1 : 2.8	1 : 2.3	1 : 1.75	1 : 1.4
5	1 : 4.0	1 : 3.2	1 : 2.7	1 : 2.0	1 : 1.6

From the curves by Purdy it is readily seen why, in Series C and D, each increase of clay above the minimum used in any one of the groups in this study should have increased the refractoriness of the glazes. In Members 1 and 2 of Series C, Groups I and II, we no doubt have the most fusible mixtures that can be obtained with these RO's. Seger (p. 236, Vol. I) found that with 0.25 K_2O and with ratio of Al_2O_3 to SiO_2 of about 1 : 6 (the same as ours) he obtained maximum fusibility with 0.5 equivalent Al_2O_3 and found that either less or more Al_2O_3 caused an increase in refractoriness. This mixture of Seger's is about the same as our II, A1.

Heat Range.—Increase of clay with constant feldspar content decreases the heat range. If additions of clay in these glazes makes them less fusible, these additions must be making the mixture more and more removed from the eutectic mixture of the compounds involved, which, by theory, should decrease the heat range in which a good glossy condition free from overfiring would be maintained. A study of these highly viscous, and in many cases incomplete, solutions checks the theory.

Opacity.—While increase in clay content in any one series increases opacity, we can not attribute this increase of opacity to the mere increase in clay, for on comparing

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corresponding glazes in the several groups we have equi-opacity with the same Al_2O_3 content whether that Al_2O_3 be derived from feldspar or from clay.

Crazing.—We have crazing only in Groups III, IV, and V, it being worse in Group V. In any series where crazing occurs, we find that it is decreased by increase of clay.

EFFECT OF FELDSPAR.

We have, in many particulars, already discussed the effect of feldspar variations, and it remains now to point out things that seem to be due more to feldspar than to any of the other constituents.

Crazing.—We find that on both bodies, we have crazing only when the feldspar is present in comparatively large amounts, *i. e.*, in Groups III, IV, V.

That crazing should increase as the K_2O is increased at the expense of CaO and ZnO is in keeping with Seger's findings, and that crazing should decrease with increase of clay is in keeping with the general experience with all types of glazes. We question, however, the reasons usually assigned for the effect which these changes in composition have on crazing. In most cases many of the physical properties of the glazes which have to do with the control of crazing have been ignored.

We note that in Groups IV and V, the glazes in Series A have so shrunk as to leave a bare border around the edges of the tile. That mixtures of feldspar and whiting should so shrink is at first thought surprising after learning that high feldspar and high whiting counteracts shrinkage in bodies (see Rieke, Nos. 37 and 38, *Sprechsaal*, 1906). In bodies, however, we do not approach the degree of fusion we have in glazes; hence, we can not argue the effect of mineral constituents on glazes from their effect on body composition.

We know from our white ware body studies that the high feldspar mixtures increase in volume when vitrifying, and from the fact that these mixtures have shrunk to the

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center of tile makes evident that they have enormous shrinkage when fusing down to glasses. Being very viscous, such strains as would be set up within different layers of the glaze by this reversal of change in volume during fusion could *not* be equalized by such annealing as is obtained with the rate at which kilns are usually cooled. Unless the coefficient of elasticity of the glaze is large enough to allow of these differential strains, the glaze must break the same as the Prince Rupert drops. Additions of clay and especially of ZnO increase the elasticity of the glaze; hence, according to our theory they ought and do decrease crazing (see Staley, Vol. XII, *Trans. A. C. S.* and Hovesdtat, "Jena Glass").

That at cone 12 the glazes high in feldspar should show craze marks next to the body but not on the surface of the glaze is confirmation of our theory. In these cases, a casual inspection would lead one to believe that the craze lines extended through all depths of the glaze, but closer inspection failed to disclose any break in their upper surfaces. That increased heat treatment should correct crazing on the upper surfaces of the glaze, and not at the lower surface is no doubt due to their high viscosity which materially decreases the rate at which reactions within the fusing glaze can take place. From these cases it would seem that these glazes containing 0.5 equivalent of feldspar would have, if completely fused, sufficient elasticity to withstand these strains.

Gloss.—The high surface tension of these highly viscous glazes results, no doubt, in a higher gloss than would otherwise be obtained. With less viscous glazes, much more complete fusion would be required to obtain a gloss equal to that shown by many of the glazes in these experiments. The high gloss on all members of Series E, Group III at cone 7, for instance, is no doubt due to this high surface tension, which results from ultra-viscosity. This may explain why the influence of clay decreasing gloss did not show in the high zinc glazes as much as it did in the high lime glazes. The effect of additions of clay on gloss is not

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so pronounced in the case of the high feldspar glazes as in those with lower feldspar. Whether this difference in gloss noted in Group V and in Group I bears any relation to differences in surface tension or of the viscosity is not plain from the data at hand.

In conclusion, we give as the best glazes for each body, the following: in these conclusions, we have considered all factors, such as gloss, crazing, color, cost, heat range, etc.

Stoneware:

III	C	(1, 2, 3)	cone 7–10
III	D	(1, 2, 3)	cone 7–10
IV	D	(1, 2)	cone 7–10

Porcelain:

III	C	(1, 2, 3)	cone 7–12
IV	D	(1, 2, 3)	cone 7–12
V	C	(3, 4)	cone 7–12

None of the porcelain glazes are up to the best that could be secured with higher SiO_2 content. It is factory experience, however, that to secure the best and brightest glazes even with the higher contents of SiO_2 a portion of the CaO of Seger's cone mixtures must be replaced by some other RO, and of these, ZnO (with K_2O and CaO) has given the best results. To obtain good porcelain glazes, therefore, the SiO_2 content of the above must be raised until the Al_2O_3–SiO_2 ratio is 1 : 8 or 1 : 10.

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CHEMICAL PORCELAIN.[1]

By GERARD A. MURRAY.

DEFINITION.

The expression "Chemical Porcelain" is intended to include all porcelain wares, such as the dishes, etc., used in the chemical laboratory, which are apt to be subjected to sudden and relatively great temperature changes.

INTRODUCTION.

Object.—The object of this investigation was to determine, if possible, some existing relation between the composition of porcelains and their ability to undergo sudden temperature changes without rupture.

References.—The only paper in ceramic literature, bearing on this subject, is one entitled "Fire-proof Porcelain" by Llewellyn Bell in Volume IX of the *Transactions of the American Ceramic Society*. Bell's object was to find a body which could be heated to redness and then plunged into cold water without injury. He made up and tested in this manner several series of bodies, and finally found that the following were able to undergo the test:

Georgia china clay	22.02	20.15	19.55
Tennessee ball clay	20.33	18.60	18.04
Flint	12.70	11.62	11.25
Feldspar	23.72	21.71	21.05
$Al_2(OH)_6$	21.18	27.90	30.10

Trials were made up as before (small crucibles by casting), biscuited at cone 2, and glazed (glaze used was cone 4 formula) at cone 12. The pieces were very white, fairly translucent, approaching in looks more nearly a true porcelain body.

Bell drew the following conclusions: "These experiments seem to show conclusively that alumina may be

[1] Thesis at the Ohio State University under the direction of Ross. C. Purdy.

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introduced directly into a pottery body with good results for certain classes of ware. The lime content should be low, not exceeding 3 per cent., and there should be a small proportion of free silica. A greater content of alumina than can be introduced from clay alone seems necessary."

In the following investigation, it was decided to attack this porcelain in a very different manner from that used by Bell, and the first question to be solved was the selection of the field to be covered.

PRESENT INVESTIGATION.

The Bodies Used.—The bodies used in this investigation were the same as described by Lester Ogden in his research on the effect of composition on the strength of porcelain.

Preparation of Slip.—At the time of making up the bodies, it was the intention of the writer to make up the pieces by some method other than casting, and for this reason the bodies were made up plastic. It now became necessary to mix these plastic bodies up to the consistency necessary for casting. A small part of each batch was, therefore, ground with water in a gallon ball mill until it went well into suspension, and was then diluted until it had a specific gravity of 1.6, as indicated by a hydrometer.

Control of Thickness of Test Piece.—Two or three preliminary pieces of each body were first cast, and the length of time determined to get about 1/16 inch thickness. Ten perfect pieces of each body were then made.

It was found that the higher the clay content of the body (the specific gravities of the slips being the same) the longer time was necessary to get the same thickness; for example, the time that the slip was allowed to remain in the dry mould was increased from one minute to about two minutes, with increase of clay from 25 per cent. to 60 per cent. The bodies high in clay were by far the easiest to make perfect pieces from, but practically no trouble was met with as long as the clay was at least 30 per cent.

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However, the body containing only 25 per cent. clay was so weak and had such small shrinkage that it was very difficult to remove the pieces from the mould without breaking them. It was found that dusting flint into the mould through a fine cloth before casting reduced this trouble by reducing the sticking. The body containing 20 per cent. clay had to be abandoned, as the pieces could not be removed from the mould even after flinting them.

Marking, etc.—The casting was done each time into dry moulds. The body number was stamped on the inside, and near the top of each crucible. The test pieces were allowed to remain in the mould from two to three hours, until they had shrunk away from the sides sufficiently to be easily removed, and were then dried in the open.

Burning.—The ware was set with the large open end resting on grog, in carefully wadded saggars, and burned with coke in kiln No. 1 of the Department of Ceramics. This kiln has two fire boxes, and the draft system is a modification of the down-draft type. Forty hours of steady firing were required to reach cone 10 in all parts of the kiln. The heat distribution was very good; cones were set in the eight corners; cone 11 was reached in the hottest and cone 10 in the coolest part of the kiln. The kiln was allowed to cool slowly.

There was practically no loss in the burning, though all the crucibles were somewhat deformed at the open end as the grog did not allow this end to shrink uniformly with the rest of the piece.

Testing.—A tray to hold forty pieces was made for testing the ware. The bottom of the tray consisted of copper screen cloth, supported by heavier iron wire. Heavy wires were also so arranged as to make it possible to handle the tray with an iron rod.

The tray, filled with test pieces, one of each composition, was placed in a gas muffle kiln just above a thermocouple in connection with a Frink pyrometer outside.

The forty trial pieces were heated up to 250° C. and then the tray was quickly taken out and set in water at

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21° C.; only the lower 3/4 inch of the outside of the crucibles came in contact with the water. The pieces were then examined carefully all over for cracks, and held up to an electric light, which showed up incipient cracks otherwise invisible. The same trial pieces were again heated up to 300° C., plunged into water and re-examined; then to 350° C.; then to 400° C.; then to 450° C.; and finally to 500° C.

In order to get average results, five whole sets of trial pieces, one of each body, were tested in the above manner.

As the above treatment broke practically all of the test pieces, it was decided to heat a fresh batch of the ware direct to 500° C. and cool suddenly with the expectation that practically all pieces would be broken. It was found, however, necessary to repeat this treatment four times before all pieces showed open cracks.

RESULTS.

Character of Cracks.—The character of the cracks developed by these two tests was quite different. In the first case, when the temperature was gradually increased, the cracks appeared almost entirely in the bottom or near the bottom of the crucible, whereas the heating and cooling direct from 500° C. caused cracks near the water line and usually parallel to it. It also seemed necessary to draw a distinction between incipient cracks and open cracks.

Incipient Cracks.—By incipient cracks are meant certain lines in the body which show up bright when held between the eye and a good light. These lines only show up this way when the surface of the crucible is wet. When the crucible is dry, they are not visible, either on the surface or when held up to a bright light.

These lines usually run radially across the bottom of the crucible and vertically up the sides. When first observed, they are rather broad and not well defined, but with repeated tests they narrow down, become sharply defined, and finally develop into open cracks.

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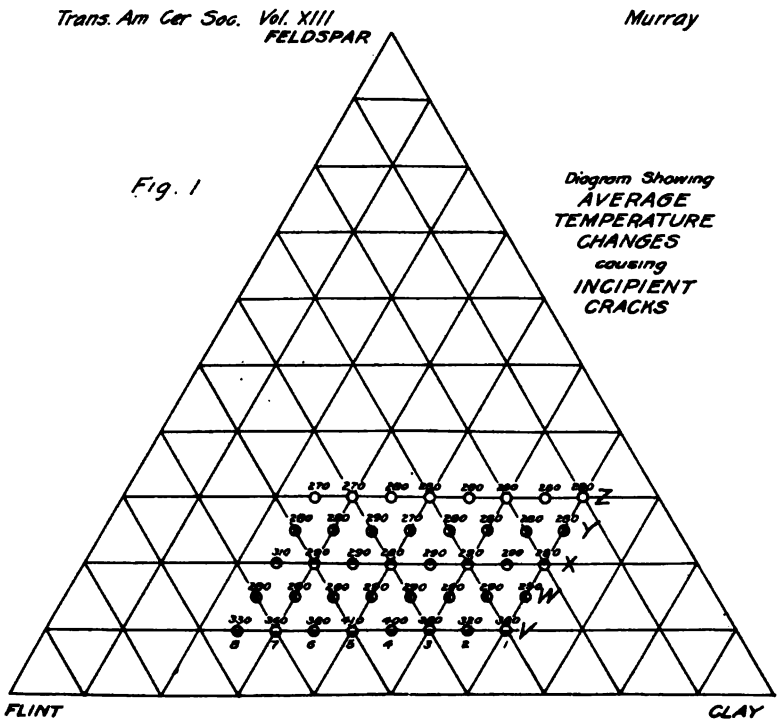

Open Cracks.—By open cracks are meant cracks which can be traced on the surface of the ware, and allow water to pass through them.

Data.—While the average figures, given in the following table, have no absolute meaning, it seems quite possible that they should be sufficiently correct to serve as a medium of comparison.

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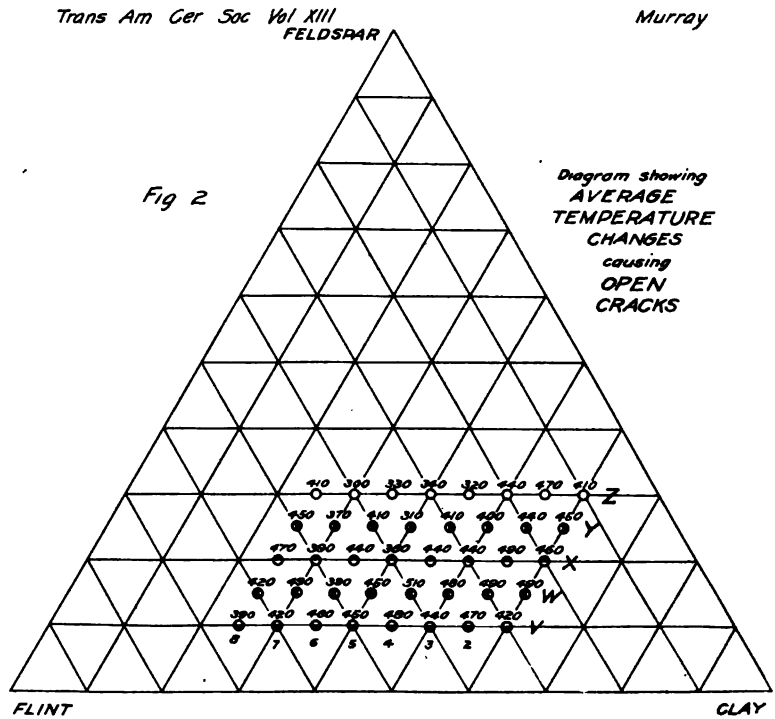

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Temperature Changes Causing Incipient Cracks.

Series	No.	1st test	2nd test	3rd test	4th test	5th test	Average
V.....	1	400	250	300	250	300	300
	2	400	250	350	250	350	320
	3	350	250	500	300	400	360
	4	350	350	500	450	350	400
	5	350	300	500	450	450	410
	6	400	300	300	550	350	380
	7	500	300	300	400	300	360
	8	300	250	300	400	400	330
W.....	1	300	300	300	250	300	290
	2	300	300	300	250	300	290
	3	300	300	300	250	300	290
	4	300	300	300	250	300	290
	5	300	300	300	250	300	290
	6	250	250	300	250	250	260
	7	350	250	250	250	300	280
	8	300	250	300	250	300	280
X.....	1	300	250	300	250	300	280
	2	300	300	300	250	300	290
	3	300	300	300	250	300	290
	4	300	300	300	250	300	290
	5	300	250	300	250	300	280
	6	300	300	300	250	300	290
	7	300	300	300	250	300	290
	8	350	300	300	300	300	310
Y.....	1	300	250	300	250	300	280
	2	300	250	300	250	300	280
	3	300	250	300	250	300	280
	4	300	250	300	250	300	280
	5	300	250	300	250	250	270
	6	300	300	300	250	300	290
	7	300	300	300	250	300	280
	8	300	250	300	250	300	280
Z.....	1	350	250	250	250	300	280
	2	300	250	300	250	300	280
	3	300	250	300	250	300	280
	4	300	250	300	250	300	280
	5	300	250	300	250	300	280
	6	300	250	300	250	300	280
	7	250	250	300	250	300	270
	8	250	250	300	250	300	270

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Temperature Changes Producing Open Cracks.

Series	No.	1st test	2nd test	3rd test	4th test	5th test	Average
V.....	1	450	300	500	400	450	420
	2	500	450	550	500	500	470
	3	350	450	500	450	450	440
	4	500	500	550	450	400	480
	5	400	400	500	500	450	450
	6	500	500	400	550	350	460
	7	550	450	300	450	350	420
	8	500	250	400	400	400	390
W.....	1	550	550	500	400	450	490
	2	550	450	500	450	500	490
	3	500	550	550	350	450	480
	4	500	550	500	500	500	510
	5	450	500	300	500	500	450
	6	250	400	450	450	400	390
	7	500	500	450	550	450	490
	8	400	400	500	400	400	420
X.....	1	500	450	450	450	450	460
	2	500	500	550	450	450	490
	3	400	450	500	400	450	440
	4	400	400	450	400	550	440
	5	400	350	400	300	350	360
	6	500	450	450	350	550	440
	7	350	450	450	350	350	390
	8	550	500	500	350	450	470
Y.....	1	550	350	450	450	450	450
	2	500	350	450	450	450	440
	3	350	300	500	400	450	400
	4	450	450	450	350	450	410
	5	300	350	350	250	300	310
	6	350	400	400	450	450	410
	7	300	350	400	350	450	370
	8	300	500	350	400	450	450
Z.....	1	350	450	300	450	500	410
	2	400	450	450	550	500	470
	3	400	450	450	450	450	440
	4	400	250	400	250	300	320
	5	300	250	450	250	450	340
	6	350	300	400	250	350	330
	7	250	300	350	250	350	300
	8	300	450	400	400	500	410

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Results Obtained by Repeated Heating to 500° C. Followed by Sudden Cooling.

Series	No.	1st test	2nd test	3rd test	4th test
V	1	checked	cracked		
	2	good	"		
	3	"	"		
	4	"	good	checked	cracked
	5	"	cracked		
	6	"	checked	cracked	
	7	cracked			
	8	"			
W	1	checked	cracked		
	2	"	checked	cracked	
	3	"	"	checked	cracked
	4	"	"	"	"
	5	cracked			
	6	checked	checked	checked	cracked
	7	"	cracked		
	8	"	"		
X	1	"	"		
	2	"	checked	cracked	
	3	"	"	checked	checked
	4	"	"	cracked	
	5	cracked			
	6	checked	cracked		
	7	"	"		
	8	"	"		
Y	1	"	"		
	2	"	"		
	3	"	"		
	4	"	checked	checked	cracked
	5	cracked			
	6	checked	cracked		
	7	cracked			
	8	checked	"		
Z	1	"	checked	checked	cracked
	2	"	"	cracked	
	3	"	cracked		
	4	cracked			
	5	checked	"		
	6	"	"		
	7	cracked			
	8	checked	checked	checked	cracked

checked = incipient cracks

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Incidental Data.

Series	No.	Per cent. absorption = $\frac{W - D}{D} \times 100$ W = saturated wt. D = dry wt.	Per cent. drying shrk. = $\frac{L_1 - L_2}{L_2} \times 100$ L_1 = plastic length L_2 = dry length	Per cent. burning shrk. = $\frac{L_2 - L_3}{L_3} \times 100$ L_3 = burned length	Relative translucency
V.....	1	9.70	3.36	8.53	3.2
	2	8.45	3.09	7.73	3.2
	3	9.60	3.09	6.18	3.1
	4	9.08	2.82	5.91	3.2
	5	8.00	2.05	5.12	3.3
	6	8.43	2.82	4.36	3.7
	7	7.45	2.04	4.59	3.8
	8	7.47	1.52	4.06	4.2
W.....	1	4.81	3.36	9.04	3.6
	2	4.69	3.36	9.04	3.3
	3	3.81	2.82	8.99	3.5
	4	3.08	3.36	9.04	4.0
	5	3.67	2.82	8.48	3.6
	6	2.84	3.63	8.29	4.1
	7	2.64	2.04	8.16	3.6
	8	2.32	2.30	7.92	4.5
X.....	1	3.60	3.63	9.84	3.2
	2	2.85	3.09	10.30	3.6
	3	2.28	3.36	11.11	4.1
	4	1.08	3.09	10.31	4.7
	5	0.58	2.30	9.46	4.8
	6	0.74	1.78	9.41	5.6
	7	0.75	2.56	8.20	5.4
	8	0.85	1.52	7.61	5.7
Y.....	1	1.39	3.89	10.65	3.8
	2	1.97	2.82	10.54	4.2
	3	0.26	2.30	9.97	4.5
	4	0.15	3.63	9.84	5.0
	5	0.36	2.56	8.71	5.3
	6	0.14	2.56	9.23	5.6
	7	0.39	2.56	8.71	5.7
	8	0.41	1.52	6.09	6.3

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Incidental Data (*Continued*).

Series	No.	Per cent. absorption = $\frac{W-D}{D} \times 100$; W = saturated wt., D = dry wt.	Per cent. drying shrk. = $\frac{L_1-L_2}{L_2} \times 100$; L_1 = plastic length, L_2 = dry length	Per cent. burning shrk. = $\frac{L_2-L_3}{L_3} \times 100$; L_3 = burned length	Relative translucency
Z.....	1	1.64	3.63	10.36	4.4
	2	0.53	3.09	10.31	4.5
	3	0.05	2.82	10.54	4.6
	4	0.05	2.82	10.54	5.5
	5	0.09	2.56	9.21	5.3
	6	0.05	2.56	8.72	5.9
	7	0.09	2.56	8.71	5.8
	8	0.18	2.30	8.44	6.5

SUMMARY.

Effect of Composition.—The results as to open cracks are rather erratic, but serve in some instances to strengthen the conclusions drawn from the other results.

A comparison of the averages of the results obtained shows that the V series, the lowest in feldspar, withstood the treatment best. This is more evident in case of the incipient cracking. Moreover, the test of repeated heating and cooling at 500° C. verifies this conclusion.

It is also evident that in both the V and W series (containing 10 and 15 per cent. feldspar, respectively) the bodies containing 40 per cent. and 45 per cent. clay show best resistance to cracking. In the X, Y and Z series (containing 20, 25 and 30 per cent. feldspar, respectively) better resistance to cracking is shown by the extreme numbers (both those high in clay and in flint) than by the intermediate numbers of the series.

Effect of Porosity.—A comparison of the above results with the absorption of the bodies shows that the bodies

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having the highest absorption (the V series) withstood the sudden cooling treatment best. It is also quite noticeable that the extreme numbers of the X, Y and Z series, which have higher absorption than the intermediate members, showed better resistance to cracking than did the intermediate members.

CONCLUSIONS.

1. Unglazed porcelain bodies, low in feldspar, undergo the test of sudden temperature changes without injury better than do the bodies high in feldspar, when burned at the same heat treatment.

2. Among the bodies low in feldspar, containing 15 per cent. or less, about 40 per cent. clay seems to give the best results.

Among the bodies higher in feldspar, above 15 per cent. high clay or high flint seem to give better results than bodies containing more nearly equal proportions of clay and flint.

3. These results may, however, be due to a difference in degree of vitrification, rather than a difference in composition, since it is very evident that, among the bodies tested, the areas of relatively high absorption withstand the test better than do the areas of low absorption.

4. In the bodies containing more than 15 per cent. feldspar, those highest in flint stood the test better than those high in clay, notwithstanding the fact that they were apparently more vitrified as shown by the absorption data. This does not seem to hold in the case of the open cracking when the feldspar is 15 per cent. or less, but apparently does hold in the case of incipient cracking. This does not agree with a statement made by Burt, p. 19, Vol. III, *Trans. A. C. S.*

5. Fom the data at hand, the writer feels unwilling to indicate any definite range of composition in these trinary mixtures best suited for the manufacture of chemical porcelain.

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STEEL DIES AS APPLIED TO THE MANUFACTURE OF DUST-PRESSED WARES.

By ALBERT E. SMITH, Trenton, N. Y.

Classification.—Dies may be divided into four classes, *viz.*, small plain, such as are used for small floor tile, door knobs and cleats; large plain, such as are used for wall tile, bricks, etc.; small complicated, such as are used for sockets, buttons, and switch boxes; large complicated, such as are used for entrance switches, panelettes, etc.

Materials.—The material used in the construction of a die depends largely on the design and the quantity of ware to be made. For small pieces that do not require sharp edges, cast iron would give fair satisfaction, but the use of cast iron dies for large wares is discouraged because of the danger of the die cracking under the pressure required to make the ware solid.

White brass and type metal are the materials used for making design or relief tile dies; steel for plain tile dies; iron with steel faces for brick; cast iron, cold rolled steel, tool steel, and cast steel for electrical porcelain and door knobs.

Hardening.—No matter of what material a die is made, unless it is hardened, it will show the wear and tear rapidly. There are several ways of hardening a die, among them being the following: (1) heating the die to a cherry-red and dipping in water; (2) heating to a cherry-red, sprinkling with cyanide of potash while in the fire, then dipping in water; (3) heating to a cherry-red and dipping in fish oil.

Every diemaker will tell you that his method of hardening is the best, but whatever means you employ to harden the die, there is always the risk of warping or cracking it. If warped, a tedious grinding process is necessary to get the die true. If cracked slightly, it might still give satisfactory results.

The hardening of a die increases its initial cost about

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Tricks of the Diemakers.—The old saying, "There are tricks in all trades" holds good with regard to diemaking. It is very easy for the diemaker to deceive you. For instance, if you specify that only the best grade of steel shall be used in the making of a die, the diemaker could use, without much risk of detection, a cheaper grade, such as cold-rolled steel, which is much easier to work. The diemaker could use solder to fill bad fits and corners, and cover up file and tool marks with solder, or frost polishing with fine emery to conceal inferior work.

One Vital Point in the Construction of a Die.—It should always be borne in mind in the construction of a die that the dust will flow downward. In view of this fact, all cups and weak places should be made in the bottom die, and, as far as possible, side holes eliminated.

Comparison of Cost between Soft and Hardened Dies of the Same Design.—In order to get a comparison of cost between soft and hardened dies, we took three dies of the same design, but of different quality. The first was made of good steel, but not hardened. The second was also of good steel, but hardened about as hard as possible without taking chances of its warping or cracking. The third was hardened in every part.

The first cost of the unhardened die was $22.50, and after making 54,000 pieces it was not fit to be repaired, making a die cost of 41.7 cents per thousand pieces. The first cost of the die of average hardness was $31.00 After making 58,500 pieces it was reparied at a cost of $11.00. After making 43,000 pieces, it was again repaired at a cost of $11.00. After making 91,000 pieces it was considered worn out. The total cost of this die was $53.00 and it produced 192,500 pieces, making an average cost of 27.5 cents per thousand.

The initial cost of the die which was hardened in every part was $35.00 and it has made to date 119,000 pieces, with a repair expense of only $2.50. The die will make about 25,000 pieces more before it needs a general repairing, making a cost of 26 cents per thousand pieces to date.

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The general repairs will cost about $15.00 and the die will then be good for the same quantity as before, making a total of 288,000 pieces at a total die cost of $52.50 or 18.2 cents per thousand pieces.

Value of Having Your Own Repair Shop.—The value of having a repair shop, the equipment of which need only consist of a small lathe, drill press, shaper, brazier, bench and tools, is in the saving of time on small repair jobs, which, in the majority of cases, could be made in the time consumed in sending the die to the outside repair shop. In this way, part of the delay in filling orders could be eliminated, besides saving a little in cost of repairs.

Should Each Factory Make Its Own Dies? Some of the points in favor of making your own dies are: (1) that you can give preference to those you need in a hurry; (2) you know what material is being used in their construction, whereas, if outside diemakers build the dies you would probably have to wait your turn and then trust to the honesty of the diemaker as to the quality of the material used.

The Care of Dies.—To get the full life of a die, it should be thoroughly cleaned after use, taking care to remove all foreign matter not only from the sides and case, but also from the pin holes.

Use of Carborundum for Dies.—We have been informed that carborundum dies are giving satisfaction in wire-drawing. I would like to ask if it is possible to get carborundum fine enough so that it could be formed and polished, thus making a possible substitute for steel in dies. If not, the hardened steel die seems to be the cheapest and most satisfactory for the making of dust-pressed wares.

DISCUSSION.

Mr. Simcoe: I would like to ask Mr. Smith what kind of steel he uses. Is it very expensive? Is it ordinary or tool steel?

Mr. Smith: Tool steel; the outside of the cast is cast iron.

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Mr. Simcoe: Where do you find the most wear in the first-class steel?

Mr. Smith: At the pin.

Mr. Simcoe: How do you harden?

Mr. Smith: Heat up in fish oil.

Mr. Lovejoy: I think the last word of the present time in dry-pressed brick manufacture is the use of a cast iron mould with a cast iron die plate, but lining the mould with tempered steel saw plate. The cost of the mould complete is comparatively low and after the steel lining is worn we throw it away. The cost of regrinding plus depreciation of a solid steel mould is more than the cost of steel plate lining.

Mr. Coulter: I am not familiar with the process of drawing wire through carborundum dies. I believe that it would be a difficult proposition to make a die of intricate shape, using carborundum. The difficulty would be to get the die so smooth that the pressed clay would come free from it readily. The simple forms would have to compete with steel and would hardly be economical.

Mr. Wilder: There are a lot of steels on the market now that are being used in other lines, much harder and last longer than tool steel. It is almost entirely discarded, for instance, in those high-speed cutters and grinders used in milling iron and steel. Tool steel will cut week in and week out without losing an edge, and I would suggest that possibly some of these steels would be suitable for dies. They are probably as easily worked as tool steel, providing a man knows how to use them.

Mr. Orton: While I approve of Mr. Wilder's suggestion, I doubt whether it would work out. The value of vanadium, nickel, chrome or any other special high-speed steel is in the fact that they will retain their cutting edge while running at a very high temperature. I do not believe these special steels will keep their edge on resistance any better than good common carbon tool steel at the temperatures of our clay dies, and they introduce a factor in handling that the common steels do not. You have to

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know more about their heat treatment in order to forge them, and the ordinary mechanic cannot be trusted to repair and dress them as he can a carbon steel tool, no matter how hard it is.

Mr. Malm: Do you form the die before you temper it?

Mr. Smith: Yes.

Mr. Malm: If so, after tempering do they warp?

Mr. Smith: Sometimes. It all depends on the mechanic. That is one reason why you cannot get satisfactory results outside of die works. If you had your own die shop you could get it done satisfactorily.

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CAUSE OF PERMANENT EXPANSION IN FIREBRICK.[1]

By JOHN MILES OGAN.

Firebrick made of certain clays expand permanently after they have been placed in a wall and subjected to intense heat treatment. The clays studied in this investigation are known in the laboratory as No. 102 and No. 103. Clay No. 102 is a semi-flint clay which is slightly plastic, and clay No. 103 is a flint clay. These clays were studied singly, and also in mixed proportions of 75 per cent., 50 per cent. and 25 per cent. of each clay with the other.

Making the Trial Pieces.—The clays were pulverized until they passed through a 16-mesh sieve. This was accomplished by crushing in a small jaw crusher and pulverizing in a ball-mill. The ball-mill was opened and the contents screened at intervals to prevent much of the clay being made finer than 16-mesh.

The percentage composition of the bodies is shown by the following table:

Body No.	A	B	C	D	E
Clay No. 102....	100%	75%	50%	25%	0%
Clay No. 103....	0%	25%	50%	75%	100%

The bodies were made up dry by weight and well mixed with a spatula while dry. Water was added until thoroughly wet, and each body was worked by hand on a plaster block until the mass was homogeneous.

Burning.—The brickettes were set on edge about 1/4 inch apart and in groups of fifteen, consisting of three of each body. The groups were drawn from the kiln at different heat treatments, draws being made at the following cones: 010, 05, 3, 7 and 13. Each group was so placed that it could be easily drawn. The cones were placed singly. The cone to which each group of brickettes was to burn was placed beside that group in a manner that

[1] Thesis at the Ohio State University under direction of Ross C. Purdy.

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it could be easily seen at all times. The burning was done in a down-draft kiln fired with coke.

Volume Determination.—The volume of each brickette was determined by Seger's volumeter before and after burning. Each brickette was weighed dry, weighed after complete saturation under a pump exhaust, and weighed while suspended in water.

True Specific Gravity Determination.—The true specific gravity of the raw clays and of the burned brickettes was determined by the pycnometer method. The material was pulverized to 100-mesh and dried in an oven at 105° C. for an hour. About three grams of the dry powder were weighed and transferred to a specific gravity bottle of known volume, boiled thirty minutes and allowed to cool to room temperature before weighing. After cooling, the bottle was filled to graduated mark and weighed.

Refractory Test.—Each of the clays deform at cone 34 in the Deville furnace.

Formlae Used.

D = Dry weight of brickettes in grams.

W = Weight in grams after complete saturation.

V_b = Volume of brickettes in cc. determined by volumeter.

V_c = Volume of the clay particles in brickette or of skeleton in the burned brickette.

V_p = Volume of pore space in brickette.

Sp. gr. = Specific gravity determined by the pycnometer.

$\frac{D}{\text{Sp. gr.}} = V_c$, true volume of clay particles.

$V_b - V_c = V_p$, volume of pore space in brickette.

$\frac{V_p}{V_b} \times 100$ = Percentage pore space.

$\frac{W-D}{V_b} \times 100$ = Percentage open pores.

$\left(\frac{V}{V_b} \times 100\right) - \left(\frac{W-D}{V_b} \times 100\right)$ = Percentage pores.

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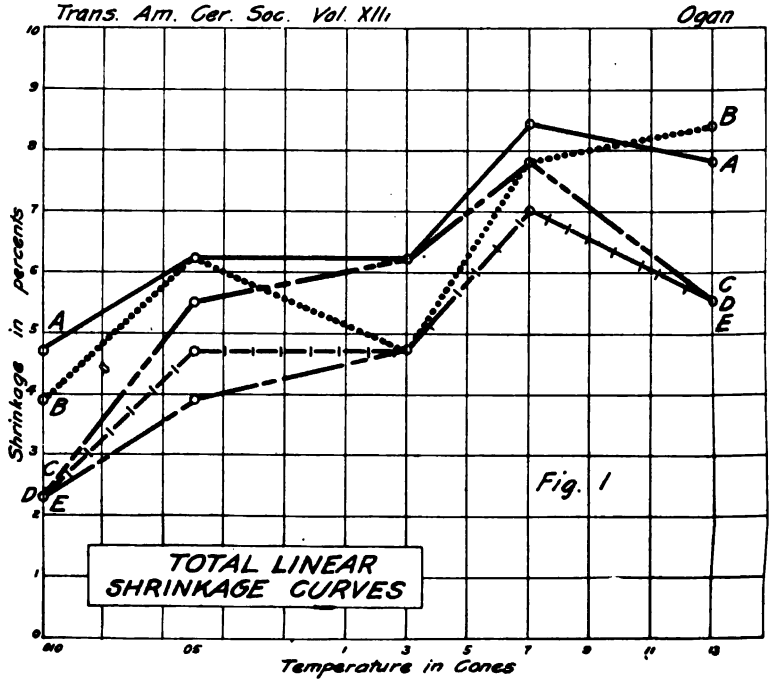
Sp. gr. = Wt. of solid powder ÷ (Wt. of water to fill empty bottle — Wt. of water to fill bottle containing solid).

Curves.—The following curves show graphically the results obtained. The shrinkage curves are drawn from the average obtained for each heat treatment by taking the average of the percentage shrinkage of three brickettes given the same heat treatment.



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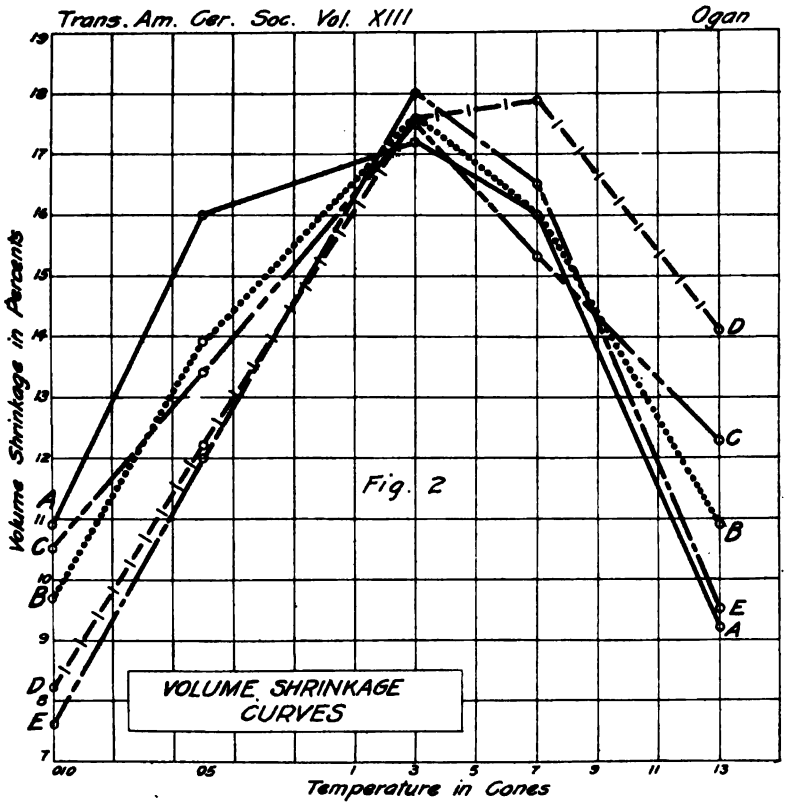

Fig. 2

SUMMARY.

Volume Shrinkage.—The volume shrinkage curve of the two clays and of their mixtures all have the same general direction. The data and curves show that the exterior volume of the brickettes decreases progressively with increasing intensity of heat treatment, reaching a minimum at cone 3, and then increases from cone 3 to cone 13. At cone 13 the size of the brickette is approximately the same as at cone 010.

The range of the volume shrinkage is at cone 010 from 7.96 per cent. to 10.9 per cent., at cone 3 from 17.2

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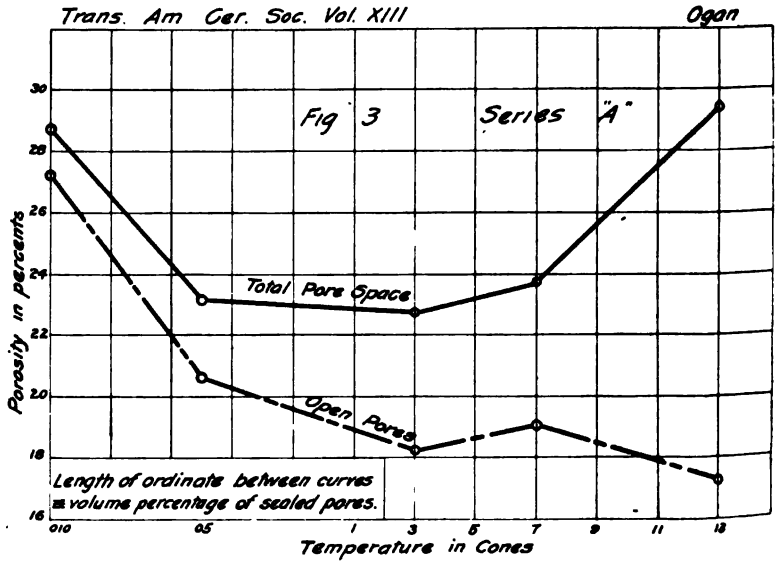
per cent. to 10.0 per cent., and at cone 13 from 9.2 per cent. to 14.1 per cent. The volume shrinkage of the clay bodies varies only 0.8 per cent. at cone 3, and probably the variation is less a little earlier than cone 3.

Clay No. 102 has a greater shrinkage at cone 010 than clay No. 103, while at cone 3, clay No. 103, the reverse of this is true and continues so until the maximum intensity of heat treatment of cone 13 is attained.

The shrinkage of the mixture of the two clays at once 010 and at cone 3 is a fair average of the shrinkage of the two clays, but at cone 13 they are all higher than the pure clays with the shrinkage greatest in the mixture high in clay No. 103.

Clay No. 103 shrinks more rapidly than clay No. 102 up to cone 3, then the rate of volume increase is about the same in each up to cone 13.



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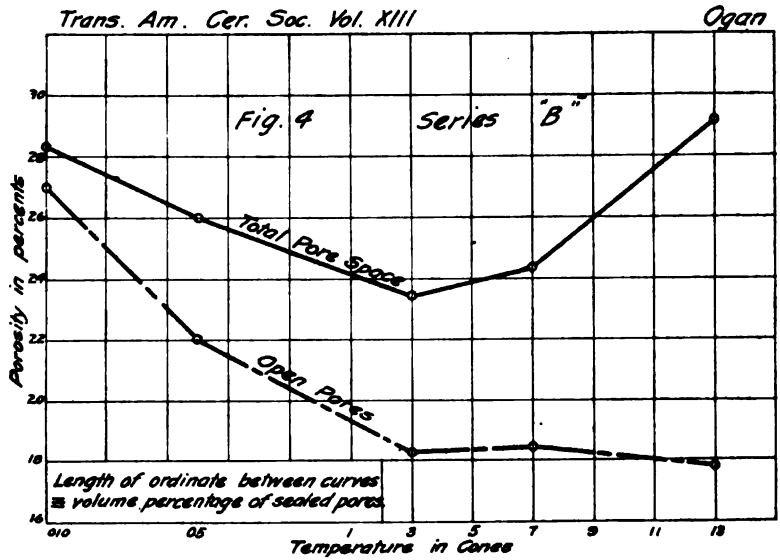

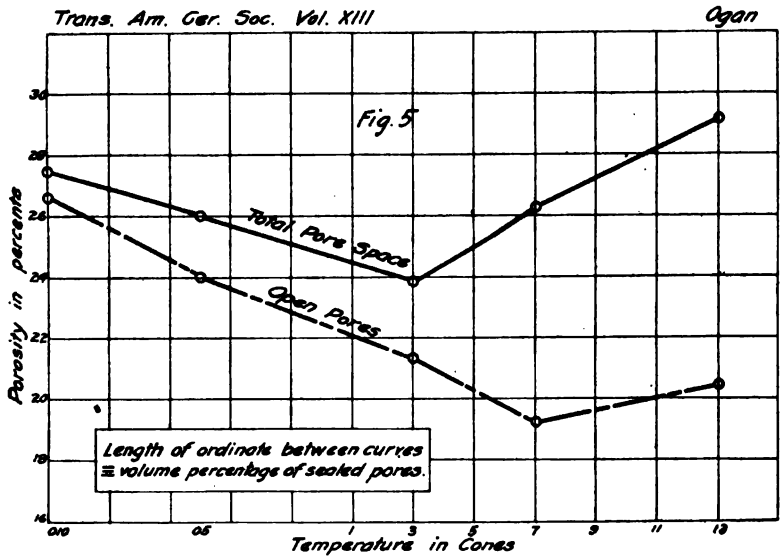

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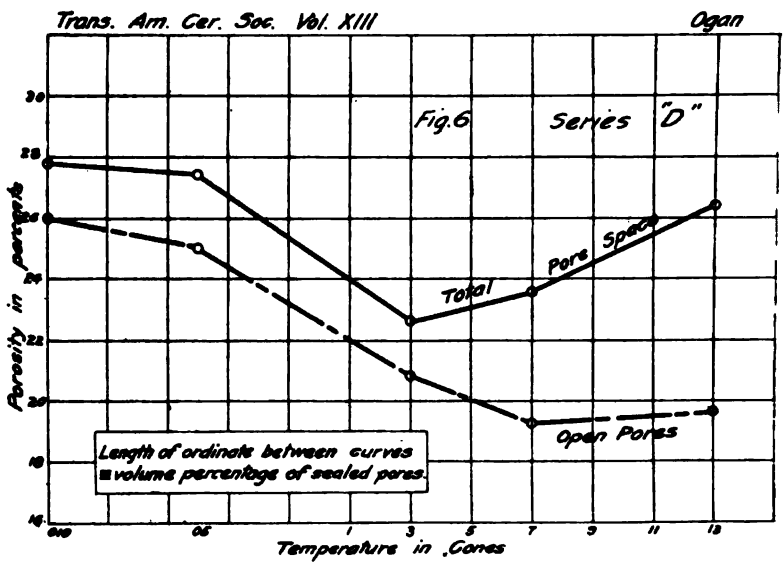

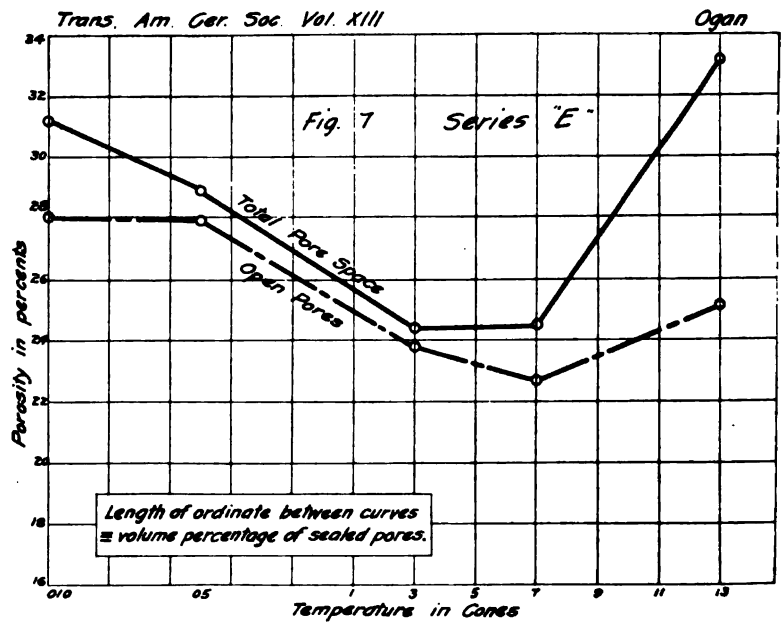

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Porosity.—The porosity data and curves show that the total pore volume decreases from cone 010 to cone 3, but increases from cone 3 to cone 13.

The volume of the open pores also decreases from cone 010 to cone 3 while the clay is shrinking, but remains fairly constant from cone 3 to cone 13.

The sealed pore volume (the difference between the total pore volume and the open pore volume) remains fairly constant up to cone 3, where the sealed pore volume begins to increase simultaneously with the exterior volume increase. From cone 7 to cone 13 the volume of the brickettes increases rapidly as does also the volume of the sealed pores, both at about the same rate.

True Specific Gravity.—The true specific gravity of the solid material in the clay bodies remains fairly constant from cone 010 to cone 3. From cone 3 to cone 13 it shows a slight increase. Clay No. 102 shows a slight decrease in the true specific gravity at cone 010 and cone 05, but has increased at cone 3.

Volume Changes.—The brickettes increase in volume from cone 3 to cone 13 and at the same time increase in porosity and, to some extent, in true specific gravity. In other words, the volume of the clay particles decreases while the volume of the brickette increases. The sealed pore volume increases rapidly from cone 7 to cone 13, while the volume of the brickette increases and the open pore volume remains fairly constant.

Soluble Salts.—When seeking a possible cause for this inflation of the brick mass, it was conjectured that some constituent of one or both of the clays was dissociated or at least volatilized, and being contained in the glassy matrix, the gas or vapor expanded with increase in temperature, forming pockets or blebs. It was readily assumed that the most easily volatilized constituents were the alkalies and that of these, those combined with the more unstable compounds (the soluble salts) would be the more readily vaporized. The data shows that only 38.0

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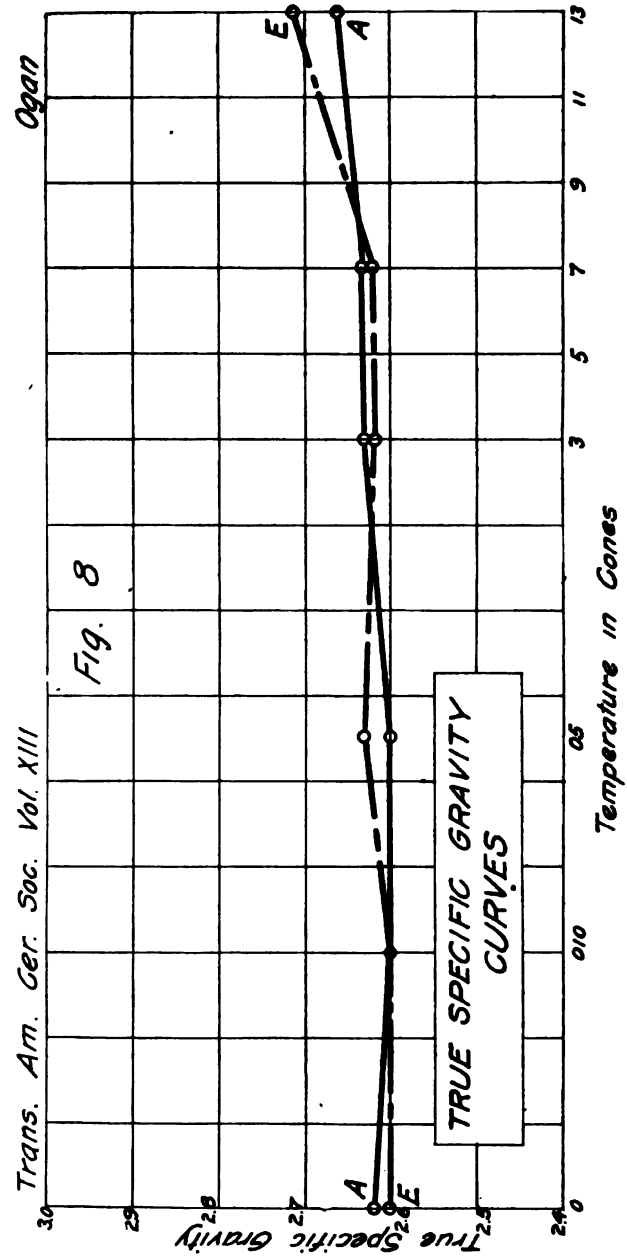

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per cent. of the total soluble salts contained by the unburned clays are "fixed" by the fusion. In fact, there is no appreciable decrease in soluble salts with increase in heat treatment, even at cone 13. While the data does not warrant positive assertion that the development of bleb structure is due to volatilization of the soluble salts, still they do not weaken the hypothesis. It is certain that the vapor pressure of some constituent of the clay is so low as to permit of its volatilization at temperatures attained in these tests and in the stoves and furnaces, causing a bloating of the fused magma and consequent swelling of the bricks.

CONCLUSION.

Since the volume of the brickettes increases at the same time and at about the same rate as the sealed pore volume increases, we may say that the sealed pores and the volume increase are closely related. Therefore, in conclusion, the permanent increase in the volume of the brickettes made of the fireclays is due to the formation of impervious bleb structure by volatilizing gases in the glassy matrix formed by fusion.

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THE OXYGEN RATIO.

By H. H. STEPHENSON.

For all practical purposes, a glaze can be explained by 6 characteristics: 3 major and 3 minor. The major characteristics are fusibility, coefficient of expansion, crystallization; the minor, elasticity, refractive index, durability (resistance to acids and atmosphere). Crazing or peeling depends chiefly on coefficient of expansion, but partly also on elasticity. A matt texture depends on the extent of crystallization, though the refractive index may conduce to a pleasant appearance.

The effort of the ceramist is, or should be, to correlate these characteristics with each other and with the chemical composition. This can be done only by eliminating all varying conditions between different workers, the most important of these being the body on which the trials are being fired. Experiments on crazing and peeling, for example, are quite useless when done on a body which may not have its like anywhere else. It is obvious, then, that scientific standards of measurement must be introduced for each characteristic of a glaze, and that the glaze must be studied apart from any body. Probably the best way to do this is to fire it in cylinders of metal, refractory glass of fused silica, and, if possible, to study only the inner core of the glaze which has not been in contact with the containing vessel. Given equal temperatures and duration of firing, the results will then be legitimately comparable.

The next step is to remove all pre-conceptions from our minds. Of these, the most common and the most pernicious is the oxygen ratio, an entirely arbitrary figure which assumes that alumina functions as a base and has three times the value of the bases, which in turn have only half the influence of the silica, and apparently may be interchanged among themselves to any extent without altering the properties of the glaze. Excluding back-numbers, I propose to take the most recent volumes of

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your *Transactions* (Vol. XII) and to show by quotation the inconsistencies to which one is exposed by using this ratio. Taking the subject of mattness, we have these enlightening remarks:

Author	Page	Quotation
Stull and Radcliffe	134	The true dividing line between clear and opalescent glazes lies on or very near to the total O. R. line of 1 : 2.
Claffin	536	Bryan's matt maturing at cones 02 to 2 has O. R. of 1 : 1.19. I obtained good matts as low as 1 : 1.13.
Claflin	536 537	Prof. Orton's curve shows that a ratio of 2.3 is necessary to obtain a matt at cone 1....All matt glazes published by Binns and designed to mature at cone 1 had O. R. lower than that specified by Orton.
Binns	543	An O. R. of 2 : 3 is, in my experience, invariable.
Singer	681	I started with a proved matt glaze of O. R. 1 : 2.
Stull	707	Dr. Singer started with a glaze of O. R. 1 : 2. Is not this the best ratio for *fusible* glazes?
Stull and Radcliffe	134	Lines of equal O. R. in which B_2O_3 is calculated either as an acid or as a base do not bear any definite relation to the dividing line between clear and opalescent glazes.

The only conclusion one can draw is that oxygen ratio has nothing to do with mattness. It would be curious if it had. Next comes coefficient of expansion, and as they have not been contradicted, we may take Stull and Radcliffe's dictum (XII, 134) on it:

"The line between crazing and non-crazing glazes does not conform to any O. R. lines whether B_2O_3 be excluded or included either as acid or base."

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Lastly, comes fusibility, and I am not aware that any one has even claimed it to be connected with the oxygen ratio.

This ratio, then, does not govern crystalline behavior, it does not govern coefficient of expansion, it does not govern fusibility. What on earth does it govern? Only, so far as I can see, the minds of ceramists. Perhaps some of these gentlemen may think it worth while to give reason for the faith that is in them.

Once prejudice is swept away, the end is in sight with regard to glazes. A matured glaze differs from a body in that the chemical reactions have proceeded to a finish; the form in which the raw materials were introduced is therefore of no consequence. This is the difference between glaze and body and it is of enormous advantage to us in studying glazes. The number of experiments necessary to obtain complete knowledge of glazes, though doubtless very large, is finite. With scientific combination we are assured of victory.

Let us for a moment endeavor to get some idea of the work to be done. A glaze may consist of some 10 constituents, each of which may be varied, for all practical purposes, by twentieths of its own amount. The number of combinations is therefore ${}^{20}C_{10}$, which gives 184,756 glazes to experiment on. These are to be tested for 6 characteristics, cone by cone, through a range of 30 cones. The total of experiments is therefore 33,256,080, which, with reasonable collaboration and the million dollars invested in ceramic training in the States, could be accomplished in 20 years. The fusibility tests at different cones would refer, of course, to duration of firing.

Bernard Shaw says that the right to live is abused unless constantly challenged, and the remark is as true of scientific theories as of men. Ceramists are languishing under an effete system, of which the two most pernicious elements are the constant reference to the oxygen ratio and the idea that glaze trials must always be conducted on bodies.

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DISCUSSION.

Mr. Orton: This gentleman's arraignment of the oxygen ratio is all right from his standpoint, but he does not seem to see what the oxygen ratio is for, or what it pretends to be. As I understand it, the oxygen ratio does not set up to be a mode of proving any visible quality. It is simply a mode of contrasting the physical peculiarities of bodies whose composition is intricate and of whose actual chemical structure we have no definite knowledge. It is a mode of comparing these, one with another. The oxygen ratio is not a theory—it is a mode of study. That is all it was ever intended to be. When dealing with substances like bodies and glazes, chiefly glazes, which are glassy combinations, and where the internal structure of the body is entirely unknown and as yet unknowable, there must be some mode of systematically comparing them. It cannot be done on the basis of percentages very well, because the mind soon becomes lost in a maze of figures. No mind is big enough to retain relationships on the necessary scale. Neither can wholly satisfactory results be obtained by the use of molecular formulae. You cannot get wholly satisfactory results by any single system. Professor Staley had a paper dealing with this subject in the first session of this meeting, only a small portion of which was read, but in it he sets forth five different systems by which these facts of chemical structure may be analyzed and compared. They have all been tried thoroughly, and they all have something of value which will lead them to be used for some time to come. No one of them is complete or final, but nevertheless, we cannot afford to lose any of them. The oxygen ratio is another instance of like kind.

I do not see how any one would imagine that in the case of two silicates of the same molecular composition and of the same oxygen ratio, such as $CaO2SiO_2$ and $PbO2SiO_2$, they would necessarily have the same melting point. That would be against the chemical nature of things. But, if you isolate a small field of silicate bodies

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for study, keeping a large part of each body constant (the bases for instance) and permitting but one variable at a time (the acid, for instance) then the oxygen ratio does become a very simple mode of contrasting the properties of the series, and to that extent it is entitled to the use and consideration of ceramists and chemists.

As a matter of fact, the ceramists did not initiate the use of this ratio. The first use of it was by the mineralogists. They were dealing with the composition and structure of intricate silicates long before ceramists took them up. They used the oxygen ratio as a means of comparing compounds which seemed to have some characteristics in common, such as the form of crystallization, uniform angle of cleavage, etc. They could not find any other method as useful for their needs as the oxygen ratio. Later, the metallurgists, being in the same situation as to s ag compositions, grasped this principle and applied it to the comparison of slags, and it has been most serviceable. Show a piece of copper ore to a metallurgist, and he will tell you the oxygen ratio of the slags he would use in smelting it. He would not presume to say that an oxygen ratio of 1 to 2 in his slag would therefore be equally satisfactory in the slag for the iron ore. It is not possible to make comparisons by oxygen ratio between dissimilar groups of silicates. It was never intended that comparisons should be attempted except between bodies having much in common.

When the third branch of silicate technology began to take form and ceramists began hunting for some mode of correlating their glasses and glazes, which are even worse than minerals, because they do not crystallize usually, they took up the oxygen ratio and used it, and it has been a great benefit to them, Mr. Stephenson's opinion to the contrary, notwithstanding.

Mr. Stephenson: I am indebted to Professor Orton for his discussion, but I should have thought that his plea for adopting the ratio from an older science would have

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been diammetrically opposed to American ideals. He does not try to harmonize the conflicting statement I quoted from the *Transactions*, nor does he justify the position of alumina among the bases.

Mr. Purdy: "Once prejudice is swept away, the end is in sight with regard to glazes" says Mr. Stephenson. Quite evidently he assumes he is without prejudice and yet from what he has had to say in this note it would appear he had all yet to learn about glazes, to say nothing about the usefulness of the oxygen ratio as a tool.

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THE BURNING TEMPERATURE OF LIMESTONES.

By A. V. BLEININGER and W. E. EMLEY.[1]

This subject is one with which primarily the lime manufacturer is concerned but which also is of some secondary interest to the ceramist who is dealing with calcium carbonate in the composition of his bodies. The subject will be discussed under three headings:

1. The minimum burning temperature of limestone.
2. The permissible maximum burning temperature.
3. The physical changes accompanying the burning of lime.

By the burning of lime we mean evidently the dissociation of the calcium and magnesium carbonate of limestone to form calcium and magnesium oxide which proceeds according to the reversible reaction:

$$CaCO_3 \rightleftarrows CaO + CO_2$$

This reaction is endothermic and evidently represents a heterogeneous equilibrium in which the gaseous concentration of $CaCO_3$ and CaO may be considered as negligible. Writing the equilibrium equation in which C_1 = molecular vapor concentration or pressure of $CaCO_3$, C_2 = that of CaO and C_3 of the carbon dioxide we have

$$\frac{C_2C_3}{C_1} = K \text{ or } C_3 = \frac{C_1}{C_2}K.$$

Since C_1, C_2, and K are constant, C_3 must also be constant and hence it is only the pressure of C_3, carbon dioxide, which governs the reaction, causing it to go forward or backward.

The heat of decomposition of calcium carbonate is usually taken to be 449 calories per kg. of carbonate or 1020 calories per kg. of carbon dioxide. The dissociation temperature of $CaCO_3$ has been the subject of a number of investigations. The earliest work along this line is

[1] By permission of the Director, Bureau of Standards.

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probably that of Debray[1] and Le Chatelier.[2] The latest work is that of Zavriev[3] and Johnston.[4] The work of the last investigator appears to be the most accurate and reliable. He found that the pressure of the carbon dioxide becomes equal to the atmospheric pressure at 898° C. which may thus be taken as the dissociation temperature of $CaCO_3$. Hence, it is not necessary theoretically to heat limestone beyond this temperature, a condition to which there are certain practical objections as will be shown later. Johnston has also correlated the dissociation pressure and temperature in the equation:

$$\log p = \frac{-9340}{T} + 1.1 \log T - 0.0012T + 8.882$$

Bearing in mind the theoretical dissociation temperature, let us examine, briefly, the conditions of dissociation which confront the manufacturer of lime. While, undoubtedly, he could burn his limestone at this temperature, the fact remains that he can not afford to do so because it would take too long a time to accomplish the desired result. It is evident that the size of the pieces of limestone is of great importance in this connection inasmuch as all of the heat must be imparted to the stone from the outside, *i. e.*, through the surface.

The rate of heat-flow from the exterior to the interior of the lump of stone depends upon the difference in temperature between the inside and the outside of the lump, the radius of the piece, assuming it to be spherical, and the heat conductivity, which probably decreases as the stone is burnt to lime. From this it follows that the higher the kiln temperature, the more rapidly will the stone be burnt, and *vice versa*. It is, hence, obvious that it is eco-

[1] Compt. rend., **64**, 603.
[2] *Ibid.*, **102**, 1243.
[3] Compt. rend., **145**, 428.
[4] Jour. Am. Chem. Soc., **32**, 938.

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nomically impossible to burn lime at the minimum temperature except for special purposes where lime of high quality is required.

The minimum dissociation temperature of a considerable number of limestones was determined, in the Pittsburg Laboratory of the Bureau of Standards, by making up small cylinders from powdered limestone, provided with a hole (in the center, and parallel to the axis) which penetrated to about the middle of the specimen. This cylinder was placed within a small tubular furnace, about two inches in diameter, heated by a coil of nickel chrome wire. The latter was attached to the inside by means of a magnesite cement coating. A thermocouple was inserted into the limestone cylinder, and another one placed in position beside the specimen so that the temperature could be measured both on the inside and the outside of the cylinder. The latter position, of course, represented the furnace temperature. By means of two rheostats the heating current was adjusted so that the time-temperature curve of the furnace space represented a straight line. Owing to the endothermic nature of the reaction, it is evident that the temperature curve of the couple within the cylinder will cease to be parallel with that on the outside during the dissociation of the calcium carbonate. The heat, penetrating from the outside to the inside, is not utilized in raising the temperature but in doing the work of dissociation. A lag, therefore, appears more or less pronounced, as the amount of carbonate is large or small, or the rate of heating slow or rapid. In Fig. 1 this lag will be at once observed. In 37 samples of limestone thus examined this lag was clearly indicated and was invariably located at 880° C., notwithstanding the differences in the physical structure of the limestones. It would seem that this point might well serve as a standardization temperature in the calibration of thermocouples. Attention might be called, however, to the fact that the readings were made direct from the millivolt meter, no potentiometer having been used.

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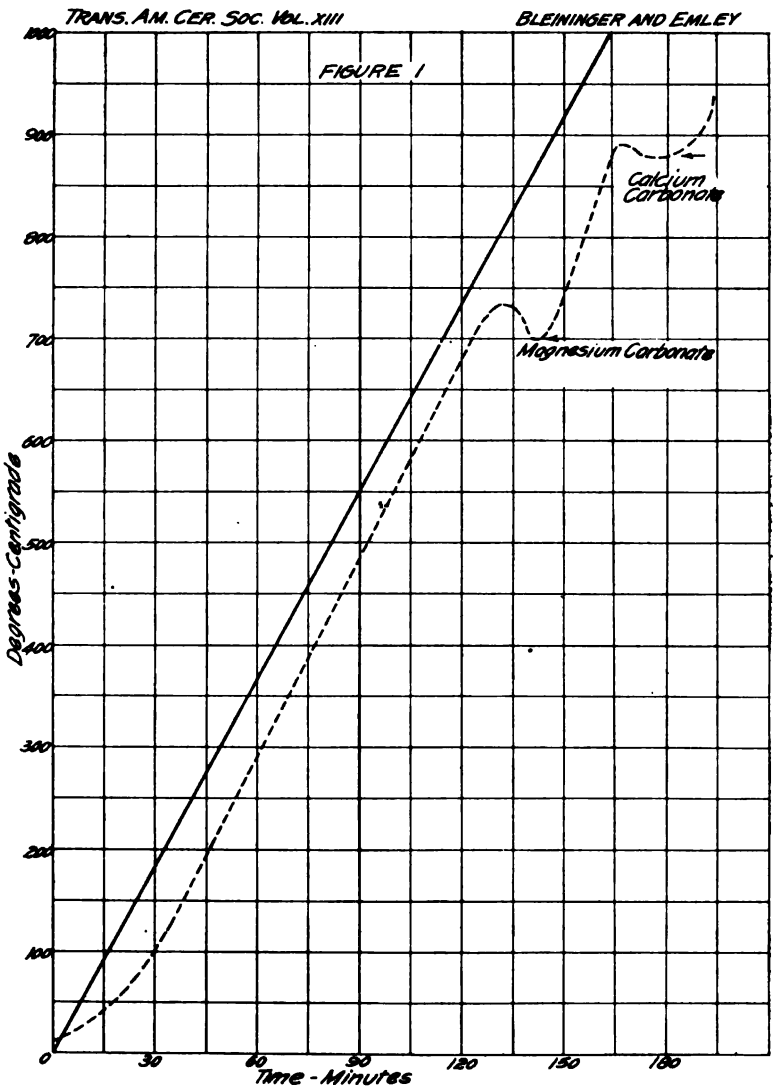

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In dealing with magnesian limestones we have, in addition, at a lower temperature, a corresponding lag point for the dissociation of the magnesium carbonate. This temperature in the present experiments seemed to be more variable though it was close to 750° C.

It would seem, then, that 880° C. (or 898° C. as determined by Johnston with more refined instruments) represents the minimum burning temperature and, providing sufficient time were allowed, all limestones could be burnt at this point. That this can not be done commercially we have already seen. While it would be desirable, as far as the tonnage output is concerned, to burn at as high a temperature as the fuel would produce, we are limited on the other side by different considerations. The impurities of limestones are evidently the varying amounts of silica, ferric oxide and alumina or those oxides capable of acting as acids in contact with a strong base. The amount of free available lime is decreased not only by the mere presence of these compounds but far more so by the amount of CaO which they are capable of fixing at the temperature involved, as silicates, ferrates or aluminates. Thus in a limestone having the composition,

Calcium carbonate	96.36	per cent.
Magnesium carbonate	0.74	"
Silica	1.41	"
Alumina	0.25	"
Ferric oxide	0.40	"

the amount of lime actually available as such might be approximated in the following manner: Assuming that tri-calcium silicate and tri-calcium aluminate are formed, we would have left $96.36 - (7.25 + 0.75) = 88.36$ per cent. calcium carbonate available to form free calcium oxide. The impurities, however, not only withdraw part of the lime from its useful function but, in addition, deteriorate the material by causing incipient softening of the stone and closing up of the pores. It is necessary to realize that just as lime and other fluxes bring about the vitrification

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of clay, so silica, alumina and iron oxide cause the partial closing up of the pores in the limestone. That this softening actually takes place may be observed when sticking occurs, in many hot going lime kilns working impure stones, *i. e.*, when the hot mass consolidates and must be started by means of iron bars. This partial condensation of the lumps of lime taking place under the same forces which bring about the vitrification of clays may, of course, be readily measured by means of the usual porosity and specific gravity determinations as they are applied with clays. Pure lime suffers some contraction in pore space at the ordinary kiln temperatures. But it cannot be overburned, a fact well known to lime manufacturers. It is evident, therefore, that limestones of this type offer no difficulty in burning and that in such lime kilns the capacity may be pushed to the limit by employing a burning temperature as high as is reached conveniently. The partial contraction of the pore space in the lime brings about changes in the physical structure which are of vital influence upon the slaking properties of the material. It is well known that the more porous a lime is, the more its capillary structure is developed, the better it slakes, and, hence, the more useful it is for all-round purposes. In the contraction due to the decrease in viscosity which causes the body to give way to the forces which tend to decrease its surface, not only is the capillary structure diminished and, in part, interrupted, but other changes take place, detrimental to the rapid absorption of water. These involve skin effects akin to glazing which necessarily oppose any admission of water.

Generally speaking, the larger the amount of the silica, iron oxide and alumina, present in the limestone, the lower will be the temperature at which the softening and subsequent contraction takes place. The maximum temperature, permissible for a certain limestone, is thus largely dependent upon its composition.

In order to determine the maximum temperature allowable for certain typical limestones collected by the

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junior writer in his field study of limestone quarries and kilns, it was decided to make use of the rate of hydration as measured by the evolution of heat. The quantity of heat generated and the rate at which it is given off depend upon the chemical composition of the lime and its physical structure due to the temperature at which it has been burned. Calcium oxide generates more heat than magnesium oxide and generates it more rapidly. If lime is underburned and some of the carbonate is still present, but little heat is given off. Similarly, if impure lime has been overburnt it is more or less inert in slaking. In either case the rate of hydration is decreased.

In the work of determining the maximum temperature above which limestones should not be burned, the following procedure was carried out: Thirty-seven samples of limestone of various compositions were broken into pieces of about the size of a walnut. About four pounds of each of the samples were placed in a fire clay saggar, washed with whiting, and all of the saggers placed in a small down-draft kiln heated by natural gas. About 18 hours were required to bring the kiln up to the desired temperature which was maintained, with a maximum variation of ten degrees, for four and one-half hours. After cooling for 12 hours, the kiln was opened and the samples removed. These were sealed, while still quite hot, in air-tight fruit jars. Seven burns were made at 800°, 900°, 1000°, 1050°, 1100°, 1200° and 1300°. The temperature was measured by means of thermo-couples placed in various parts of the kiln.

The rate of hydration was determined in a calorimeter. A weighed amount of the pulverized lime sample and a constant amount of water were introduced into a brass cylinder provided with a water-tight cap and a rotating stirrer. The cylinder was then immersed in the water of the calorimeter and its temperature determined before and after the hydration. From the time-temperature curves thus obtained, the rate of hydration was estimated. The latter was characteristic for different types of limes.

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In Fig. 2 (Curve 1) the most rapid rate of hydration is shown by properly burned high calcium lime. An overburned lime of this kind (Curve 2) takes twice as long to finish hydration as the normally burned specimen and, at the same time, does not evolve more than 3/4 of the heat given off by the latter. A dolomitic lime burnt to its proper temperature (Curve 3) shows a considerably slower rate of hydration than the corresponding high calcium stone. Such curves as these were obtained for every burning temperature of each lime; that is, seven curves for every material. By inspection or by the calculation of a hydration factor produced by the product of two values, namely, the temperature rise times the rate of hydration, the limiting temperature may be estimated. The temperature rise evidently is the difference between the initial and the final thermometer reading, while the rate of hydration corresponds to the temperature rise divided by the time in minutes. In Fig. 3 the effect of the burning temperature upon the rate of hydration may be observed. It would lead too far to consider the conditions of each of the 259 time-temperature curves and it suffices to state that the following limiting temperatures, above which the limes should not be burned, might be deduced.

High calcium lime, low in impurities, 1300° C., and above.

High calcium lime, high in impurities according to the amount of the latter, 1050° C.–1150° C.

Magnesium lime, low in impurities, 1000° C.–1050° C.

Magnesium lime, high in impurities, 900° C.–1020° C.

From what has already been said it will be seen that the character of the impurities has much to do with the matter of maximum temperature. Concretionary iron, such as iron sulphide, irregularly distributed throughout the stone will not manifest itself in the same manner as would finely divided iron oxide. The latter, undoubtedly, exerts a more injurious effect as regards the limiting temperature and the resulting quality of the lime.

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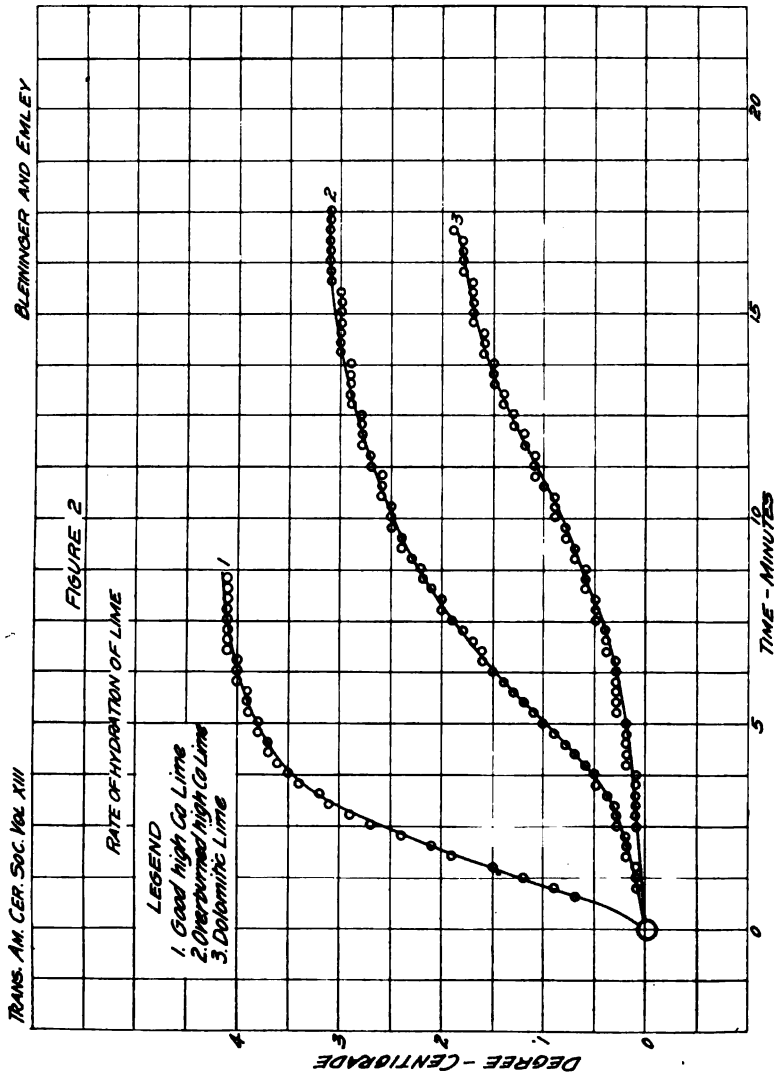

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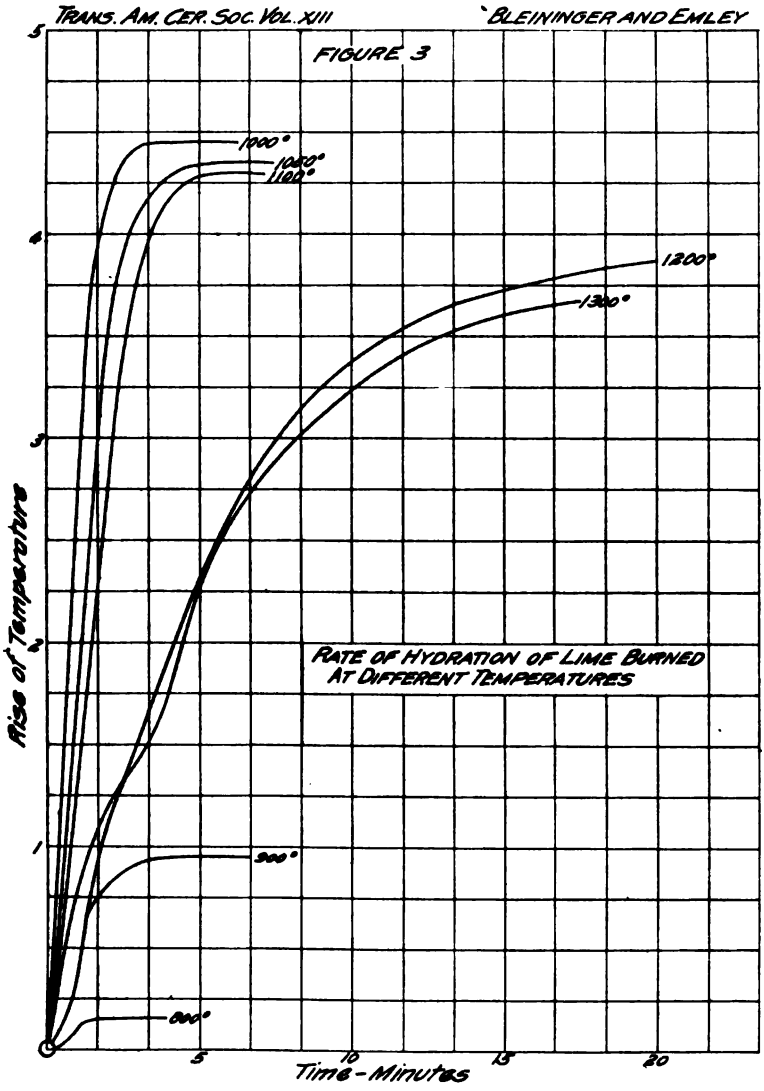

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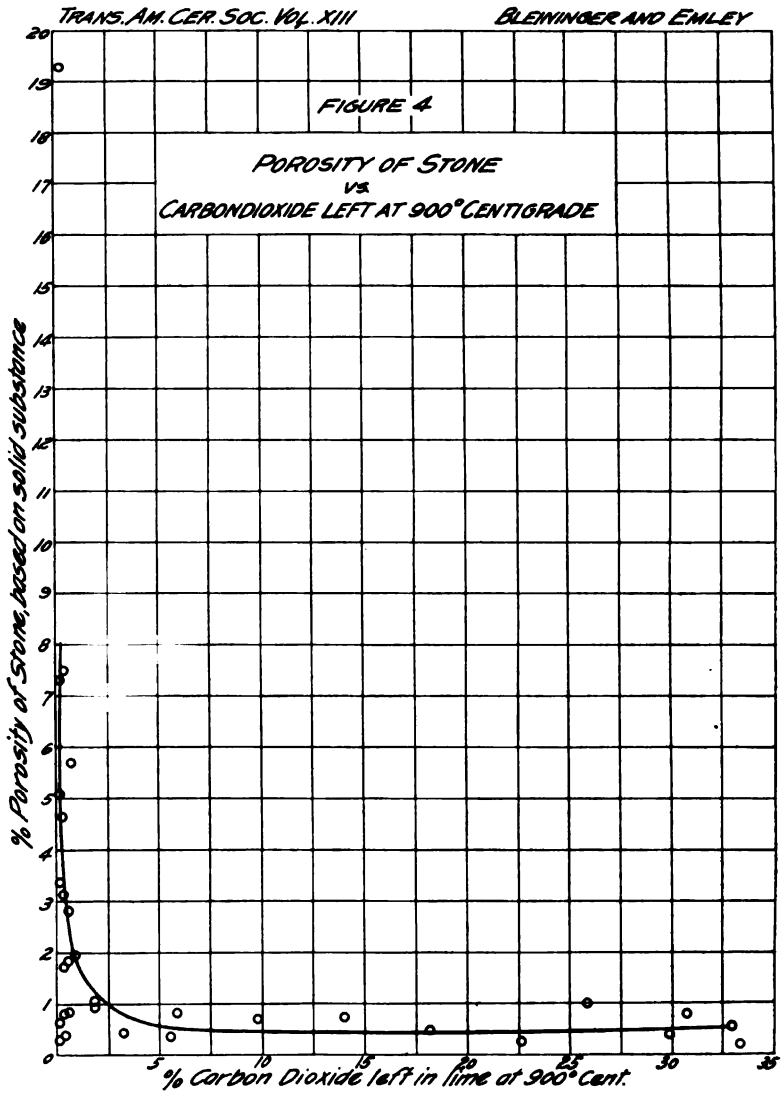

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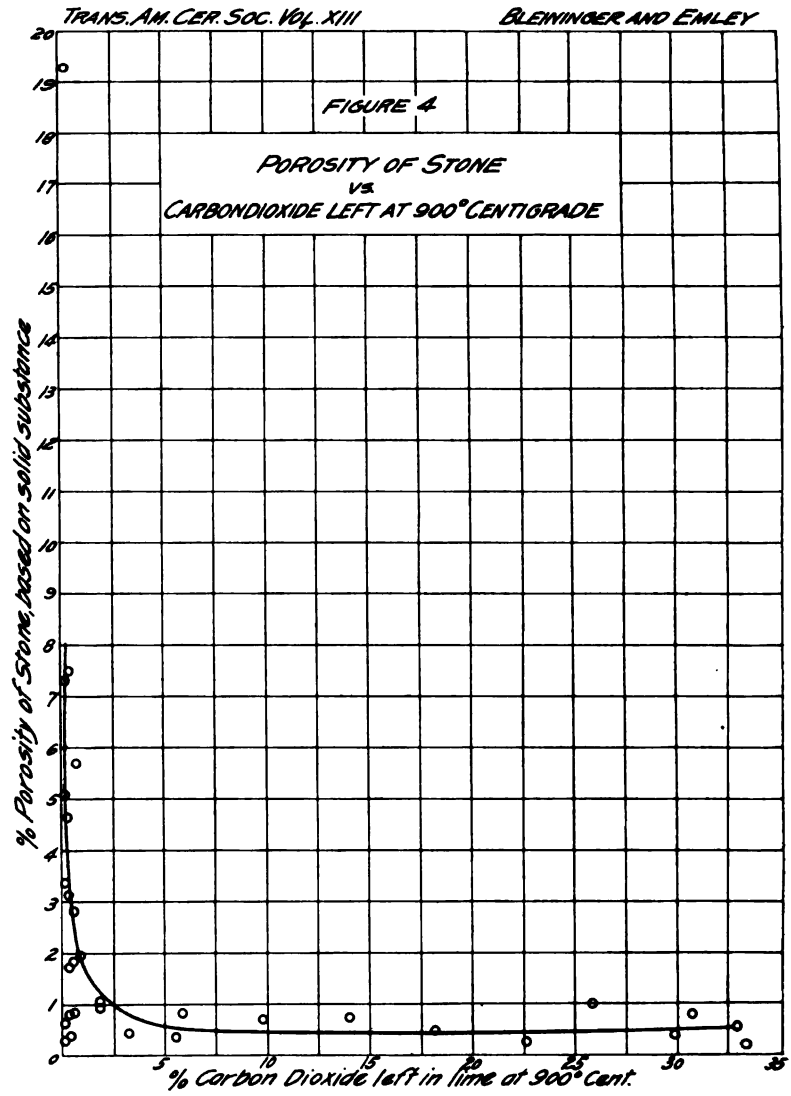

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It is a curious fact that the initial porosity of the limestone has an important bearing upon the limiting burning temperature. This is indicated very clearly by Fig. 4 in which the porosity of the raw stone is correlated with the amount of CO_2 left in the stone at 900° C. From this correlation it is clear that the more porous the stone is to start with, the lower will be its burning temperature, as measured by the residual carbon dioxide content. This is a very interesting fact, the practical bearing of which is obvious.

In order to trace the molecular changes which limes undergo upon being heated to different temperatures, careful determinations were made of the specific gravity of the lime itself and its porosity in the lump condition expressed both in terms of the volume of the true substance and of the apparent volume. In determining the densities of limes, the lump samples were immersed in melted paraffine under vacuum until the pores were sealed. The lump density was then obtained by suspension in kerosine. From these figures and the specific gravities of the powdered lime, the porosities were calculated according to the relation:

$$\text{per cent. porosity based on total lump} = \frac{\text{sp. gr. of powder} - \text{density of lump}}{\text{sp. gr. of powder}}$$

In Table I the results of these determinations are given and in Table II the chemical analyses referring to these samples of limestone, which represent typical American materials in commercial use.

In analyzing this mass of data it is necessary to consider (*a*) the density of the lime itself without regard to the lump structure and (*b*) the change in porosity with increasing temperatures.

(*a*) Some interesting relations are brought out in the study of the stones burnt to different temperatures. These

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Table II.

Analyses of Limestones.

No.	SiO_2	Al_2O_3	Fe_2O_3	$CaCO_3$	$MgCO_3$	Total
1	2.41	0.22	0.40	85.18	11.72	99.93
2	1.29	0.15	0.35	95.91	2.27	99.97
3	0.44	0.08	0.20	98.05	1.30	100.07
4	0.34	0.19	0.28	58.20	41.16	100.17
5	0.85	0.06	0.20	96.70	2.04	99.85
6	1.21	0.41	0.45	95.70	2.25	100.02
7	0.81	0.56	0.47	54.68	43.66	100.17
8	0.91	0.09	0.30	63.02	35.78	100.10
9	2.27	0.51	0.40	53.16	43.89	100.23
10	0.94	0.15	0.45	54.09	44.58	100.21
11	0.53	0.04	0.05	99.21	0.74	100.57
12	0.14	0.02	0.10	98.73	1.01	100.00
13	0.27	0.07	0.30	86.43	12.98	100.05
14	0.15	0.10	0.15	99.02	0.57	99.99
15	1.41	0.25	0.40	96.36	1.55	99.97
16	0.42	0.07	0.32	97.20	2.02	100.03
17	0.36	0.07	0.22	96.07	3.26	99.98
18	0.46	0.06	0.20	89.20	10.14	100.06
19	0.28	0.16	0.20	98.50	0.78	99.92
20	0.80	0.10	0.35	97.05	1.72	100.02
21	1.05	0.40	0.55	96.21	1.76	99.97
22	1.64	0.33	0.31	94.39	3.42	100.09
23	0.16	0.13	0.06	98.93	0.76	100.04
24	0.23	0.08	0.20	98.25	1.26	100.02
25	0.65	0.05	0.30	84.50	14.53	100.03
26	0.34	0.02	0.15	56.79	42.92	100.22
27	1.92	0.03	0.30	54.04	43.81	100.10
28	1.23	0.19	0.50	94.38	3.74	100.04
29	0.56	0.05	0.20	55.00	44.31	100.12
30	1.04	0.05	0.25	54.25	44.52	100.51
31	1.12	0.06	0.40	54.82	43.79	100.19
32	0.55	0.24	0.40	55.09	43.91	100.19
33	0.21	0.04	0.10	98.45	1.28	100.08
34	0.32	0.13	0.30	98.29	1.05	100.09
35	0.21	0.06	0.15	98.89	0.67	99.98
36	0.26	0.02	0.20	98.84	0.65	99.97
37	1.35	0.53	0.40	94.89	3.05	100.22
38	0.10	..	0.05	99.05	0.88	100.08

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are best illustrated by means of the four curves of Fig. 5. These represent four different types of limestone: number 14 is a pure high calcium limestone, number 6 an impure high calcium stone, number 26 a pure dolomite and number 31 an impure dolomite. The pure high calcium stone becomes denser with increasing burning temperature and at 1300° C. it reaches a density of 3.35. The impure high calcium stone does not do this but its increase in density begins to fall off and at 1200° C. it takes a drop, behaving in exactly the opposite manner from the pure stone. This is equivalent to saying that the true volume of the pure stone contracts as it is being raised to these temperatures while the impure high calcium stone expands. It is at once evident that the same conditions prevail which have been observed in the study of clays. It appears likely that the impurities and the lime form silicates, aluminates, and ferrates, which expand when vitrified. This, then, is the reason why pure limes constantly gain in density on being heated, while impure high-calcium limes decrease in density.

The density of the pure dolomite stone increases up to 900° C. when it reaches 3.395, then drops to 3.330 at 1100°, from where it again increases to 3.435 at 1200°. Just what this drop at 1100° means we are not yet prepared to say. It is evident that this change is a significant and important one, and it may involve some action between the lime and magnesia which we do not yet understand. As regards the impure dolomite, we again have the characteristic drop in density from 1100° to 1300° C. which corresponds to an expansion in the true volume of the mass of about 3.16 per cent.

(*b*) With reference to the porosity curves of the various limes, the changes resulting upon burning might be illustrated by typical curves, Figs. 6, 7 and 8. In Fig. 6 it is seen that the porosity increases to a maximum as the carbon dioxide gas is expelled and then decreases as the impurities enter into combination with the calcium oxide to form compounds which tend to soften and to fill

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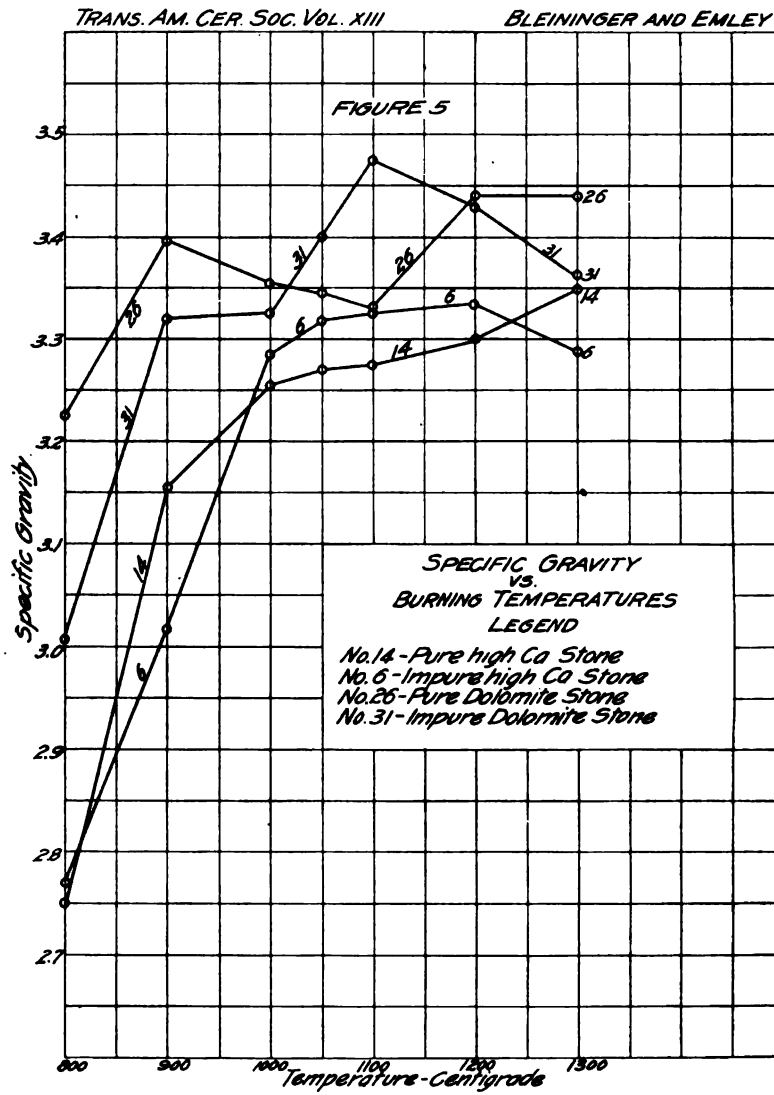

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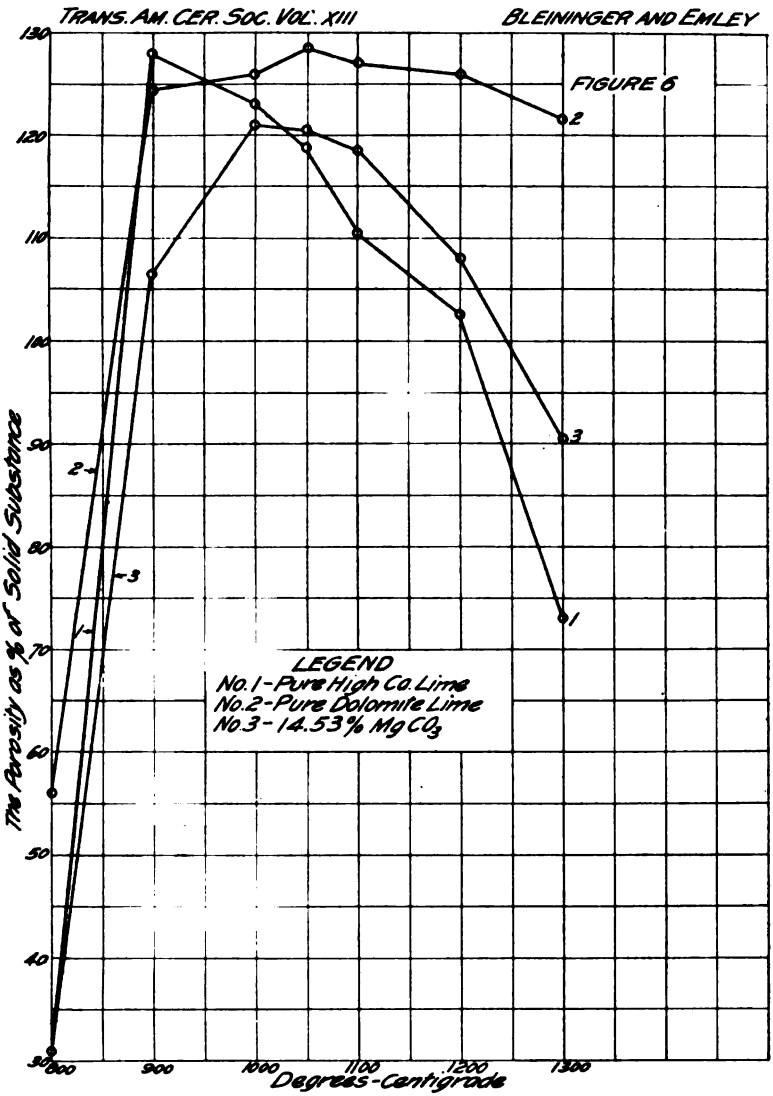

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up the pores. The most favorable condition for the slaking of the lime is when it is most porous. The more extensive and better developed the capillary system is, the more rapidly will slaking proceed, other things being equal. It must be kept in mind, therefore, that the point of maximum porosity stands for the most favorable burning temperature as far as the quality of the lime is concerned.

It is noted that the porosity increases up to a temperature of about 1000° C. where a halt occurs. These limes evidently are at their best at this temperature and their quality at higher temperatures can never be the same. An inspection of this curve will indicate that the slope from the point of maximum porosity towards the right, *i. e.*, towards the higher temperatures, is exceedingly important. The steeper it is, the more narrow is the temperature range allowable for a given stone, the more easily is it overburnt. This test, therefore, produces a means of determining the burning behavior of a stone, just as it indicates similar characteristics in clays. The angle made by the curve descending from its highest point towards the right with the horizontal gives a measure of the burning tendency. The greater this angle or its tangent, the greater must be the tendency to become dense, and, hence, the lower the quality of the resulting lime. This contraction in volume is not to be ascribed solely to the content of impurities but in a large measure this phenomenon is inherently connected with the physical structure of the amorphous lime. Thus, even certain practically pure limes condense in a most striking manner, and, on the other hand, many pure limes show practically no poral contraction. The reduction in porosity is, therefore, due, in part, to the kind of amorphous structure or the kind of colloid, and, in part, to the presence of fluxing impurities. The effect of the latter, therefore, is more marked in some limestones than in others.

It is not likely that the best burning temperature exceeds 1050° C. Any increase in porosity beyond this temperature must be ascribed to other causes, such as

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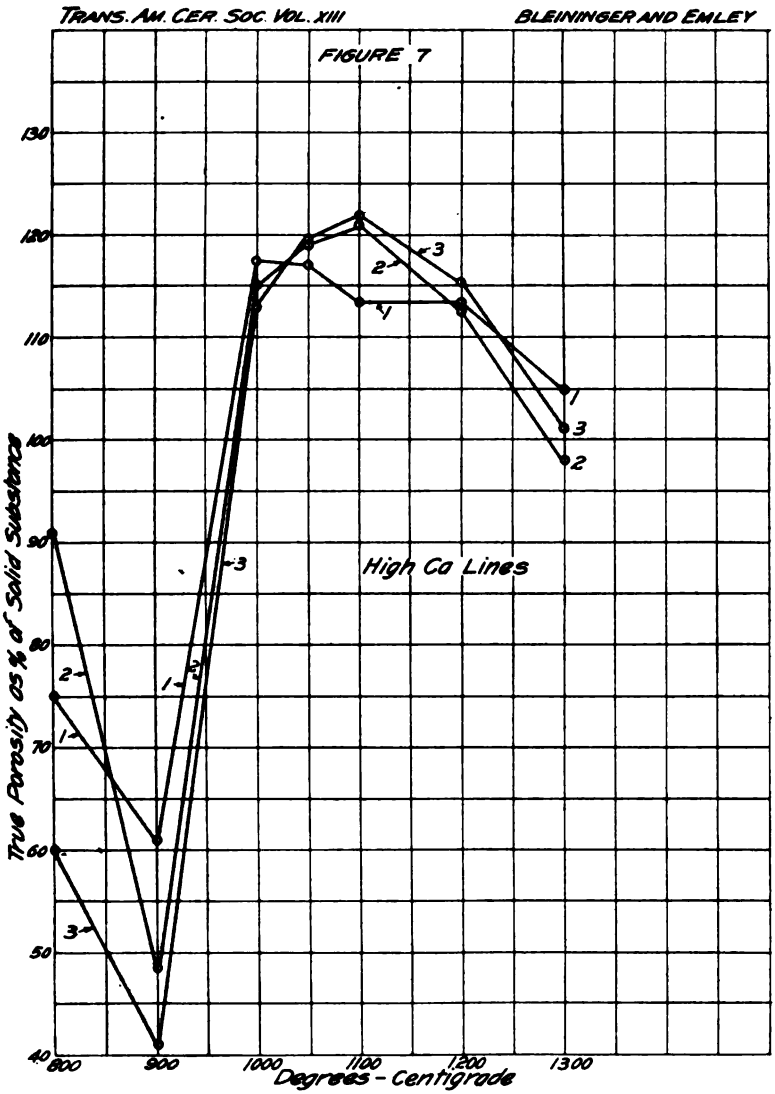

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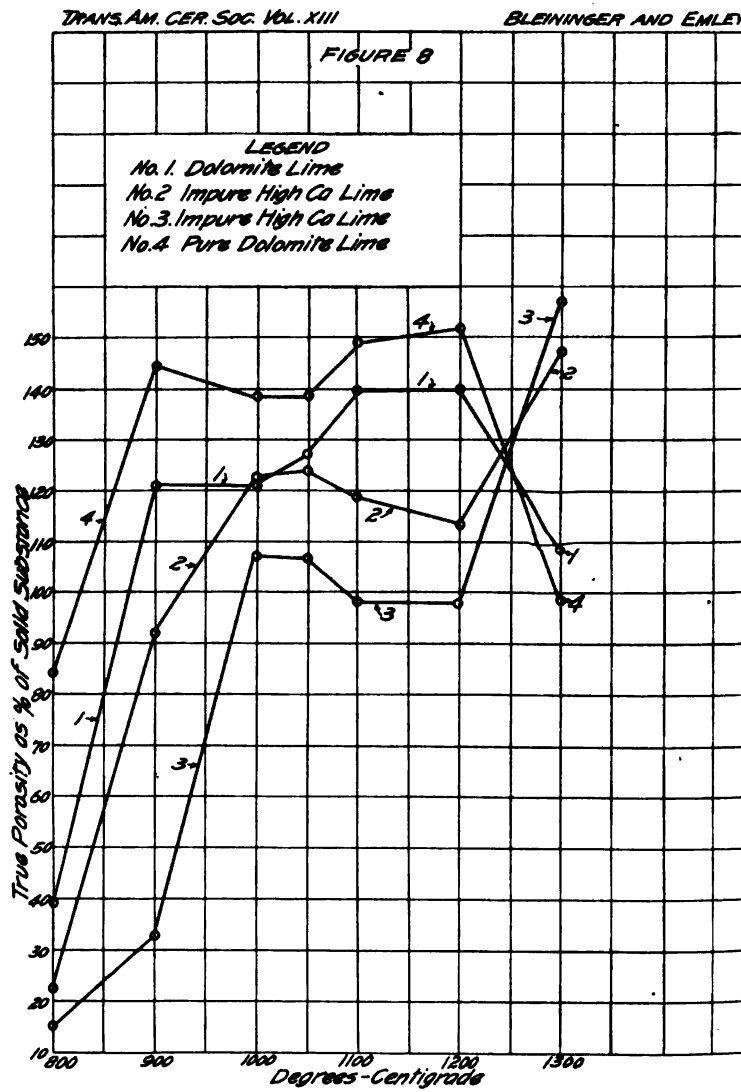

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bloating. Thus, the carbon invariably found in limestones which, in the nature of the case, cannot be oxidized completely, may cause an increase in pore space when given an opportunity to burn out at a rate too rapid to permit of the ready escape of the resulting gases. This bloating is more likely to occur in stones of a dense structure.

In Fig. 7, a curious drop in the porosities of the limes is observed between 800° and 900° C. for which no explanation is offered at the present time. In Fig. 8 it would seem that Curves 2 and 3 represent abnormal conditions and it might be suggested that we have here a case of bloating, a condition which is more likely to take place in impure stones apt to become dense or "glazed" on the surface when heated to higher temperatures. Curves Nos. 4 and 1 represent the peculiar conformation suggested by the corresponding density curves for which no explanation is offered.

SUMMARY.

1. The minimum dissociation temperature of calcium carbonate was found to be 880° C., and of magnesium carbonate 750° C.

2. The limiting burning temperature of lime may be determined from the study of the hydration curves of limes burnt at different temperatures. In these, the temperature rise of a certain weight of water heated by the slaking of a given amount of lime is plotted against time. This method, therefore, offers a means of fixing the proper burning temperature for a given lime.

3. The maximum temperature permissible for pure high calcium stones is above 1300° C., for impure high calcium stones it lies between 1050° and 1150° C., for pure magnesian stone between 1000° and 1050° and for impure magnesian stone between 900° and 1020°.

4. The porosity-temperature curve of a lime, likewise, gives valuable information in regard to the best burning temperature which is represented by the point of maximum

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porosity. The slope of the curve from this point towards higher temperature is a significant measure of the over-burning. The steeper the slope, the greater this tendency and *vice versa*. The reduction in the porosity of lime as the temperature increases is due, in part, to the inherent contraction of the amorphous substance, in part, to the fluxing effect of the impurities.

5. The more porous a limestone is in its natural condition, the more easily will it burn, that is, the more rapidly and at a lower temperature. Porous stone may be completely burnt at 900° while the denser stone requires at least 1000° C. in the same length of time.

6. The density curve of a lime burnt at different temperatures expresses its degree of purity. The specific gravity curve of pure limes tends to rise with increasing temperature above 1100° C., while the curve of the impure stone is depressed. In the case of dolomitic limes it is likely that conditions are more complex than they are in the case of the high calcium stones, due to unexplained changes.

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THE QUESTION BOX.

"What Is the Best Form of Magnetic Separator for Removing Iron from Slip?"

Mr. Purdy: Electromagnet separator. If, for any reason, the current shuts down and the magnet is not working, the stream is cut off. It works automatically. Of course, the electromagnet will load itself with iron, the same as the horseshoe, but it is stronger, more positive and under better regulation.

Mr. Simcoe: My idea of a separator is simply to have a wheel with a plate, so constructed that this plate will go through the slip and be magnetized while the slip is passing it. A series of wheels can be made, so that there will be a number of magnets in the slip at all times; and there will be an arrangement to regulate the electricity so as to connect the magnet while it is in the slip, and to throw it out of connection when it is out of the slip. The speed of the current often is sufficient to detach some of the iron and carry it over. Therefore, I plan to have a jet of water to cleanse the magnets all the time.

Mr. Mayer: We use an electromagnet. It is absolutely fool-proof. You cannot get it wrong. Just as soon as the current is off and there is no electricity in the magnet, the slip is shut off; and simultaneously, the bridge drops and lets the slip fall into another tank. We have just received two machines from the Rapid Electric Co., of Birmingham, England. One is for slip and the other for flint. This is a long trough in which the slip passes over a series of magnets. There is an electromagnet with an armature connected with the bridge. As soon as the current fails, the bridge comes down, and the slip falls through instead of going into the trough.

In our other machine, it not only shuts off the stream, but at the same time it closes the stop-cock that supplies the slip. Therefore, it shuts off the slip in two places, and it really fills the bill as an absolutely fool-proof machine. We took it out only because the magnets were

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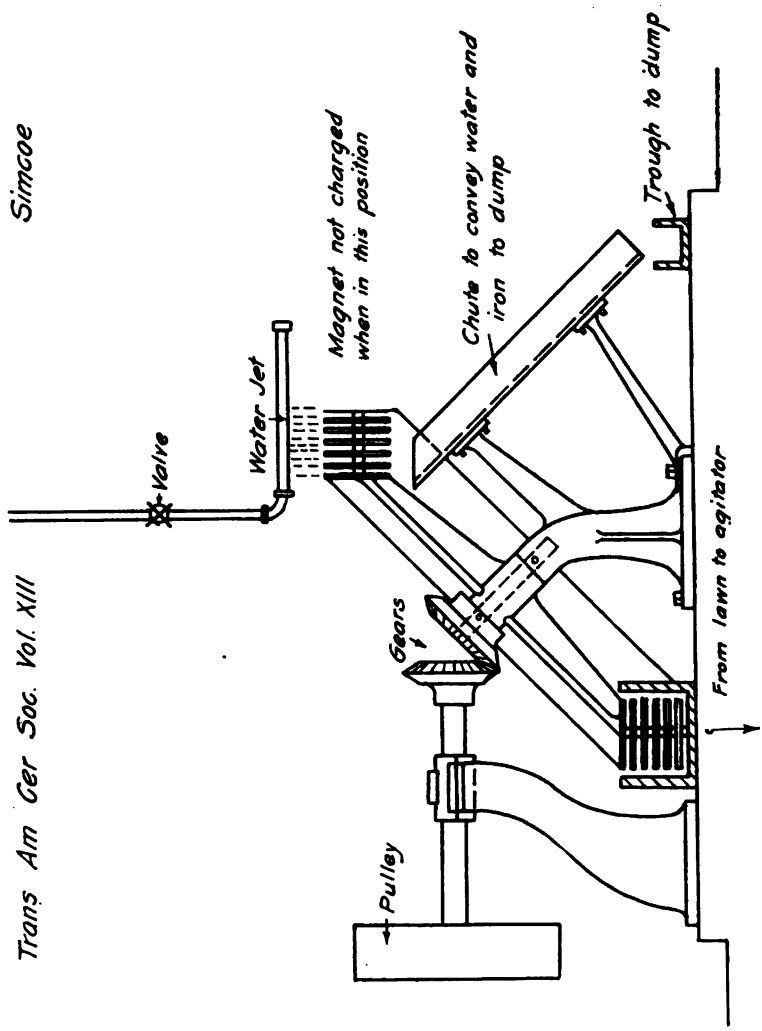

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not strong enough, but this machine that we have now is not at all expensive, and I believe that it is a good machine.

Mr. Riddle: Mr. Walker recently showed me a set of magnets he is using in his factory at Beaver Falls. It is an ingenious device. A series of electric magnets are placed in a trough with riffles arranged in it in such a manner that the slip passes under a magnet then over a partition, down under the next magnet over another partition and so on past a dozen magnets and partitions. Iron which fails to be attracted by one magnet is pretty sure to be caught on one of the following magnets. The device is so arranged that it gives a signal when the current fails. I believe it also stops the flow of slip.

Mr. Lee: In the magnetic separator, shown by Simcoe, the current of slip is continuous while there is a break between the contacts. In metallurgy, where the current should be continuous, they have a device which, I think, you could get details of from Dr. Richards, of Boston. A magnet that would revolve like that one there, but with slight points of separation, so that a point of the second magnet would be in the solution always, and not leave the hanging condition of iron, would be a great advantage; and they have a machine of that kind. You cannot handle slip with a static machine, which is the best method of eliminating iron from dry powder.

"What Is the Best Substance to Prevent Clay Slip from Settling in the Casting Process? What Is the Effect of this Substance on the Body in Firing?"

Mr. Purdy: Silicate of soda.

Mr. Barringer: I should like to ask Mr. Purdy whether silicate of soda would be good for general use. Added to some bodies it would seem to me that silicate of soda might be precipitated by bases present, thus forming an insoluble double silicate.

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Mr. Purdy: I know that silicate of soda is good to keep bodies from sticking to molds.

Mr. Watts: My knowledge is confined to a few experimental tests covering work presented by Dr. J. W. Mellor and others in Vol. VI, *Transactions of the English Ceramic Society*. The data presented by these gentlemen is, however, apparently very roughly, if at all, relative, since the value found for the standard slip, without any salt added, varied during the experiments from 11.5 to 19.5.

I made tests using silicate of soda, carbonate of potash, and carbonate of soda, and came to the general conclusion that silicate of soda was as good as any of the others, though carbonate of soda is considered by some people to be superior to the silicate. It does not possess certain faults that they claim silicate introduces into the firing process. I, however, have never had experience with difficulties in firing with bodies containing silicate of soda.

Mr. Weelans: I should like to ask Mr. Purdy whether he has noticed any peculiarity in firing due to the use of silicate of soda? Did it have any effect on the density of the body? Did it assist in vitrification?

Mr. Purdy: To some extent, yes. It made the body more rigid and more dense when burnt. You do not use an amount sufficient to cause much earlier fusion because of the silicate of soda.

Mr. Weelans: Then you would not change the body at all?

Mr. Purdy: No.

Mr. Binns: I understand that a common method in the preparation of the slip would be to blunge up and then, by subsidence, draw the water off. But, on the other hand, in the use of any alkaline solution it is necessary to add a measured amount of water to the clay, and the addition of alkali enables you to produce a thick slip with but a small amount of water. If you take an ordinary slip and blunge it in the usual way, with plenty of water, the alkali

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has very little effect. The water is already there. If you make it thin, the same process of subsidence takes place, and you reach a point where the clay will not subside any more, because of the alkali in the fluid. The use of alkali would involve an entire change in the preparation of slip for casting.

Mr. Mayer: I have never used this commercially, so do not know much about it, but I have made experiments with casting, and have come to the conclusion that you cannot mix a body up direct. I have found that if you are going to get the full effect of silicate of soda, which should be used with carbonate of soda, you had better dry the clay first, and then put this mixture in. I got some splendid results in casting some very thick pieces in this manner. I do not know whether I could get such results commercially.

I could get absolutely no good results when, for instance, I mixed up feldspar and china clay and ball clay, and put in the silicate and bicarbonate of soda while the clay was wet. I had to dry the clay first.

Mr. Purdy: I should like to ask Mr. Weelans what effect silicate of soda would have on the body in the burning?

Mr. Weelans: Just the effect that you have stated—increase its rigidity, density, and vitrification somewhat, but not to any great extent, that is, if you do not put in too much.

With reference to the use of these and other like substances in the manufacture of pottery, would say that in my experience their chief source of help lies in the following:

Effect in Clay State.

1. Used properly (as explained by Mr. Meyer and others) less water is required in the mix.

2. It toughens the clay slip, permitting it to dry freer from cracks.

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3. It dries very hard and strong, and owing to this there is noticeably less breakage of the ware in the clay state.

4. Its principal use is confined to the ware to be casted although it can be used in pressed ware (meaning in a stiff mud state permitting it to be pressed into moulds by the hands of the operator), but owing to the inconvenience in its use in pressed ware and its less pronounced benefits, it is not in general use.

5. It permits certain complicated articles being made in fewer separate pieces, hence fewer seams, resulting in less loss.

6. In casting these large pieces, though very materially assisted by the use of the above material, much difficulty is observed in securing articles free from air holes, blebs, etc.

Some of the Noticeable Results after Firing.

1. When a sufficient quantity is used to be of benefit in the clay state, in the firing, increased vitrification is noticeable.

2. Ware made up with this mixture is much more sensitive to over-firing.

3. Ware made with this mixture added to the body is, after firing, less tough, and, owing to this increased brittleness, is less durable.

4. Being more sensitive to over-firing, this condition is less easily detected in the biscuit state than in ware made regularly without this material added.

5. When ware in which this material is incorporated is over-fired, the tendency is to bring about early disintegration of the body and glaze, sometimes noticeable shortly after coming out of the gloss kiln, and sometimes not until after installation of the article (showing numerous cracks all over the piece).

This defect has not yet been positively located to

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bodies high in clay or high in flint, but the writer's limited experience would attribute it as most likely to occur in bodies high in clay.

In conclusion, I would say that for small articles the benefits derived from the use of this material in the body overbalances its resulting defects; but for heavier complicated articles not enough has been done nor time sufficient been given to fully determine its benefits.

SAGGAR BREAKAGE.

(*a*) Best system to keep track of it. (*b*) How to figure the percentage of breakage. (*c*) Has the shape any influence on the breakage? (*d*) At what stage of cooling is breakage most liable to occur? (*e*) Is the breakage on machine-made saggars greater than on hand-made?"

Mr. Barringer: Taking the last point first—"Is the breakage on machine-made saggars greater than on hand-made?" I would say that in our work with electrical porcelain, we think the breakage is greater with hand-made saggars, because there is a decided tendency for them to break where they are joined. The bottom being put on separately in the hand-made saggar, it will part from the ring; and where the ring is joined, the saggar will often break apart. Since we have used the machine-made saggars, though we have almost as much breakage, it does not appear so decidedly in these places; and any break that may occur is not so great.

I think the breakage is greater in the first ring where the rate of heating up and cooling is greatest; likewise, right in front of the door. When the door is opened, which is done very quickly after the kiln is fired, a greater percentage of saggars will be found broken in front of it than elsewhere. Therefore, the rate of cooling and heating has a decided effect on the breakage.

Regarding the shape of the saggar, we can only reckon on the same basis, *i. e.*, what we actually obtain in practice.

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Our rectangular saggars last much better than the round ones. I have not thought much about the reason.

As to the percentage, we have to use blanket figures. We know how many saggars enter the kiln, and how many broken ones come out. They run up to 20 per cent., the average life of a saggar being five burns.

Mr. Mayer: The best system for keeping track of saggar breakage, I think, and the one that we have adopted, is to have at the kiln-door a card on which are printed the names of all the different kinds of saggars we make. Whenever a saggar is thrown out, the man in charge scores it on the card. You are all aware of the fact that the loss on the drawing day does not represent the loss in the kiln. Some saggars are broken in drawing and represent a loss during placing. We also keep close track of these by the same method, the foreman making a mark for every saggar broken. The sheet is then handed in when the kiln goes in. The plan is very simple, and we have followed it for a long time, finding it a very good one.

As to how to figure the percentage of breakage, they say that any figures will lie, but our percentage of breakage on the glost is practically 10 per cent. (9.6 per cent. actual) and 5 per cent. (4.8 per cent. actual) on the biscuit. These figures vary but little, unless we run into some bad clay or something of that kind. We have maintained these figures for very many years.

By 10 per cent., I mean the ratio of saggars broken in placing and drawing to the whole number of saggars in the kiln.

We do not know the influence of the shape, because we use only the oval; but we find a much greater percentage of breakage among the saggars of low sides than among those with higher. In the saggar that we call a low cup saggar, there will be a much higher percentage of breakage than in higher ones, for the reason that the lower the saggar, the harder it seems to be to keep it straight in drying.

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"At what stage of cooling is breakage most liable to occur?" I am unable to answer. The saggars in the first ring, of course, go much sooner than those in any other part of the kiln.

"Is the breakage on machine-made saggars greater than on hand-made?" I have used nothing but hand-made, so cannot answer.

Mr. Humphrey: With reference to the last part of this subject—"Is the breakage on machine-made saggars greater than on hand-made?" I would say that my experience differs from that of Mr. Barringer's considerably. This may be due, first, to the fact that the machines were different; and secondly, to the size of the saggar. The machine-made small saggar, I believe, can be made much more readily than can a large saggar, single or double banjo; and the result is quite different. As a saggarmaker makes a saggar by hand, he re-enforces it at the point where the side joins the body, which should be the strongest point, as most of the strain comes there. In the machine-made, with which I had my experience, the saggar was not stronger at that point; and in releasing it from the drum, it was quite readily strained just at the point where it should be strongest. The result was that it would break more readily if made by the machine than it would if made by hand. If the saggarmaker had used ordinary care in doing the joining, this might not have been the result. I have not taken up the question of the comparative cost of the two kinds, but the breakage was greater in the machine-made than in the hand-made.

Mr. Burt: In fine porcelain, as long as the porcelain is at red heat, one does not hesitate to let cold air rush in; but when it approaches the point where the red heat is passing off, the kiln is sealed up to protect it. I have seen a kiln of terra cotta drawn very hot, and as soon as it got out, you could hear it crack. I have always considered that the cold air does not hurt the ware so long as it is at red heat, but the minute it passes into the next stage, there is the real danger.

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THE CHEMISTRY OF SAND-LIME BRICK.

By T. R. ERNEST, PH.D., Spokane, Wash.

The chemistry of sand-lime brick, like that of Portland cement, is a subject about which we know but little and find it easy to speculate. The literature of this new industry is at yet very meagre, and what has appeared has had to do almost wholly with the technology of manufacture, tests, etc.

In his original patents, Dr. Michaelis claimed that a hydrated calcium silicate was formed when an intimate mixture of lime and silica were subjected to the action of high pressure steam for several hours, and so far as the chemistry of this process is concerned, we have learned but very little since the time of its origin.

The work embodied in this paper was done at the University of Illinois by the writer under the direction of Prof. S. W. Parr, for the degree of Doctor of Philosophy in Chemistry, during the years 1908–1910. A more complete report of the investigation will be found in Bulletin No. 17 of the Geological Survey of Illinois.

Two general methods of attack were available for this investigation, *viz.*: Chemical and Microscopic.

In preparing the compounds for chemical analysis two general lines were followed. In one of these, a small percentage of lime was used with a large amount of silica, and in the other, a small percentage of very fine silica was mixed with a large amount of lime. By thorough mixing and long steaming it was possible to cause one of the constituents to enter almost completely into combination. This procedure simplified the process of analysis quite materially and enabled us to obtain a fair degree of accuracy in the determination of the composition of the compounds formed in the reaction.

The materials used in the microscopic study of this subject were prepared with the same degree of care as were those used in the chemical analyses. These materials were examined both in the form of thin sections and as powders properly mounted.

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MATERIALS AND METHODS.

The lime used in this work was Kahlbaum's best calcium oxide, burned from pure marble. It was carefully slaked, great care being exercised to prevent carbonation.

The silica was prepared by precipitation from sodium silicate. This material, after drying and washing, proved to be a very fine-grained and pure product.

Two grades of sand were prepared by grinding crushed quartz and Ottawa Standard sand in a disk pulverizer, sieving out the part passing an eighty- and retained on an hundred and twenty-mesh sieve, and washing carefully with acids and alkalies to remove any impurities.

For chemical analyses, samples were made by mixing the proper materials in the dry condition, then adding water and pouring into a metal dish which was then placed in an autoclave and steamed.

In those experiments in which small percentages of lime were used it was found that it practically all entered into combination with the silica. The problem was then one of the separation of free and combined silica. Where large percentages of lime were employed the silica was practically all combined, and the problem was one of the removal of the free lime without the decomposition of the calcium silicates. Various devices were resorted to in order to effect this separation, some of which will be briefly described below.

The first attempts at removing this excess of free lime were by washing with distilled water, but owing to the slight solubility of lime in water and the difficulty of keeping out carbon dioxide it was found that this method could not be used to advantage. The next attempt was to wash out the free lime with dilute acetic acid. The freshly prepared compound was placed in a beaker with water from which the carbon dioxide had been previously expelled by boiling. A few drops of phenolphthalein were then added and dilute acetic acid was added very slowly so that the solution did not become acid during

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the operation. By this procedure it seemed probable that the free lime could be removed before the acid would attack the calcium silicate. It was found, however, that even with the greatest care some of the silicate was always decomposed, but as the silica in this case was left in the form of flocculent silicic acid it was possible to remove this by careful decantation.

When it was discovered that even dilute acetic acid had the power of decomposing these silicates so easily, a search was made for a weaker acid. The ionization constants of some of the weaker acids are given in the following table:

Ionization Constants at 18°

Boric[1] $H_2BO_3^- + H^+$	1.7×10^{-9}
Hydrosulphide ion[1] $S^{--} + H^+$	1.2×10^{-15}
Hydrosulphic[1] $HS + H^+$	9.1×10^{-8}
Hydrocarbonate[1] $CO_3^{--} + H^+$	6.0×10^{-11}
Carbonic[1] $HCO_3^- + H^+$	3.0×10^{-7}
Acetic[1] $C_2H_3O_2^- + H^+$	1.8×10^{-5}
Phenol[2] $C_6H_5O^- + H$	1.3×10^{-10}

To be of any value in the removal of free lime from the calcium silicates, as in this case, it is essential that the reagent in question be without action on the silicate and at the same time form a soluble compound with lime. Both phenol and hydrogen sulphide fulfil these requirements. Of these, the latter appeared to be the more convenient and was used in these experiments. The material from which the free lime was to be removed was placed in a flask and water added. This was then connected with a supply of hydrogen sulphide gas and kept saturated for several days. This converted the lime into calcium acid sulphide without any apparent action on the calcium silicate. The silicate could then be washed and analyzed.

The action of carbonic acid on these compounds was

[1] Jour. Am. Chem. Soc., 31, p. 760 (1908).
[2] Zeitschr. physik. Chem., 32, p. 137 (1900).

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also studied and the conclusion made that calcium silicates of this character are completely decomposed by the action of carbonic acid.

METHODS OF ANALYSIS.

In the case of samples made up with an excess of lime, after the removal of the free lime, the analyses were carried out in the usual manner, *i. e.*, the silica was determined by treating with hydrochloric acid and evaporating several times. In the filtrate from the silica determination, the calcium was determined by precipitation as the oxalate and titration with permanganate.

In those samples where excess of sand was employed, it was necessary to separate the combined and free silica. The work of Lunge[1] and Millberg shows conclusively that in order to make this separation quantitative the quartz grains must be of such a size that they will settle out of water quickly. With "dust fine" quartz, these investigators found that in a two-hour digestion on the water bath, even a one per cent. solution of sodium carbonate dissolved 2.10 per cent. of the quartz taken for the test. With a 15 per cent. solution of either sodium or potassium carbonate, on the other hand, only a very slight trace was dissolved by a two-hour digestion of a quartz of such size that it would settle out of water quickly. Hydrated silicates, such as trass, opal, pozzoulane, etc., dissolved almost completely with the same treatment. The work of these investigators proves conclusively that it is necessary to use quartz grains having an appreciable size.

It might be supposed that silicates of the sort here studied would dissolve completely in acid, but the separation of combined silica is not so easily effected. On the addition of a strong acid the silicate is decomposed, the calcium going into solution as a salt of the corresponding acid, and with the separation of silicic acid, some of which goes into solution while the remainder is precipitated as a

[1] Z. angew. Chem., pp. 393 and 425.

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colloid. The amount remaining in solution will depend very largely on the concentration of the acid used. A strong acid will precipitate much of the silica which had been in solution, while a very dilute acid will retain the larger part of it in solution, but in any case there are appreciable amounts of it thrown out, especially upon heating. Hence the necessity of following any acid treatment with an alkaline solvent under conditions such that any separated silica may be redissolved without at the same time attacking and carrying into solution a part of the silica that had not been in combination.

The determinations in this work were made by first treating the sample to be analyzed with a solution of hydrochloric acid made by diluting the strong acid (1.19 sp. gr.) to ten times its volume with distilled water. The sample was broken up in a manner not to further reduce the size of the sand particles, treated with 250 cc. of this dilute acid and digested on the water bath for several hours.

The solution was then filtered off and the residue washed several times with a 5 per cent. solution of sodium carbonate, a digestion of about an hour on the water bath being employed with each washing. The sand could then be weighed after the burning of the filter paper, and the silica determined in the filtrate in the usual manner. The calcium was left in the filtrate from the silica determinations and was determined by precipitating as the oxalate and titrating with permanganate.

Where free lime was found in any quantity it was necessary to remove this or determine the amount present before proceeding with the silica determination. It can be removed by treating with hydrogen sulphide in which case the calcium is converted to the sulphide or acid sulphide, and can be removed by washing. Care must be taken to use water that does not contain carbonic acid as calcium carbonate would be thrown down by this reagent. In case the free lime is to be determined, this can be done by allowing the material to stand in a closed flask with dis-

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tilled water, which, with an occasional shaking, will dissolve the lime, when an aliquot part can be drawn off and the lime titrated with standard acid. If there is very much lime present, the sample taken should be small or some sugar added to the solution to increase the solubility of the lime. Other methods might be used in special cases, but these appear to be very satisfactory for all ordinary cases.

RESULTS OF CHEMICAL ANALYSES.

Silicate No. I.

This sample was made with three parts of lime to one of precipitated silica. Steaming was at 12–15 atmospheres per sq. in. for 10 hours, and the excess lime was removed, first by decantation of the flocculent calcium hydrate, then treating with phenolphthalein and dilute acetic acid.

Lime-silica ratio: 0.674/1.

Silicate No. II.

This sample was made by mixing three parts of sand, prepared from crushed quartz, with one part of lime hydrate. The steaming was at 12–15 atmospheres for 8 hours, and the excess lime was removed by treatment with dilute acetic acid.

Lime-silica ratio: 0.899/1.

Silicate No. III.

This sample was made in substantially the same way as sample No. II.

Lime-silica ratio: 0870/1.

Silicate No. IV.

This sample was made with 10 per cent. of CaO and the same fine-grained sand as above. Steaming was at 12–15 atmospheres for 8 hours. Lime was washed out with dilute acetic acid.

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Lime-silica ratio: 0.863/1.
Water-silica ratio: 0.632/1.

Silicate No. V.

This sample was made with 15 per cent. CaO and the fine quartz sand. Steaming was for 8 hours at 15 atmospheres. The excess lime was removed by boiling with additions of a solution of ferric chloride. This caused the precipitation of ferric hydroxide, the lime at the same time going into solution as the chloride. As the ferric hydroxide was of a very flocculent nature, it could be easily decanted off with the supernatant liquid. The process was carried on until the clear liquid showed no color with phenolphthalein. The analysis was carried out as usual except that iron had to be removed before determining the calcium.

Lime-silica ratio: 0.890/1.
Water-silica ratio: 0.508/1.

Silicate No. VI.

This sample was made with three parts of lime to one of precipitated silica. The ingredients were mixed with water to the consistency of a thick cream or slurry and steamed for 8 hours at a pressure of 12–15 atmospheres. The excess lime was removed by agitating and decanting the flocculent lime hydrate, and finally by the addition of phenolphthalein and acetic acid, and washing.

Lime-silica ratio: 0.847/1.

Silicate No. VII.

This sample was made with 10 per cent. CaO and the fine quartz sand used before. It was steamed for 8 hours at a pressure of 15 atmospheres. The lime was practically all in combination.

Lime-silica ratio: 0.818/1.

Silicate No. VIII.

This sample was made with $3^3/_4$ per cent. CaO and

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fine sand from crushed quartz. Steaming for 8 hours at 12–15 atmospheres.

Lime-silica ratio: 0.873/1.

Water-silica ratio: 0.726/1.

Silicate No. IX.

This sample was made with 7.5 per cent. of CaO and the fine quartz sand used before. Steaming for 8 hours at a pressure of 12–15 atmospheres. Only a trace of free lime remained.

Lime-silica ratio: 0.837/1.

Water-silica ratio: 0.837/1.

Silicate No. X.

This sample was made by using 8.5 per cent. CaO in the same way as in silicate No. VIII. Steaming for 8 hours at 12–15 atmospheres. Free lime was negligible.

Lime-silica ratio: 0.853/1.

Water-silica ratio: 0.824/1.

During the hardening of this sample water collected in the dish and on this a crust was formed. This material dissolved completely in dilute hydrochloric acid and showed a lime-silica ratio of 0.968/1.

Silicate No. XI.

This sample was made by using 15 per cent. CaO and fine quartz sand as in No. V. The free lime was removed by the use of ferric chloride as in sample No. V. The sample was dried and separated into two parts, fine and coarse, by means of sieves. Analysis showed the following results:

Coarse.	Fine.
Lime-silica ratio: 0.910/1.	Lime-silica ratio: 0.833/1.
Water-silica ratio: 0.544/1.	

Silicate No. XII.

This silicate was made with 7.5 per cent. CaO and the

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fine sand prepared from Ottawa Standard sand. Steaming was for 8 hours at a pressure of 12–15 atmospheres.

Lime-silica ratio: 0.887/1.

Water-silica ratio: 0.748/1.

A portion of this sample was ground in a mortar with a soft pestle so as to remove the compound from the sand grains as much as possible. The part passing an 80-mesh sieve and retained on a 120- was subjected to a process of fractionation by the use of a heavy solution. Three fractions were taken and the heavy and light fractions analyzed.

Lime-silica ratio of heavy fraction: 0.885/1.

Lime-silica ratio of light fraction: 0.830/1.

Silicate No. XIII.

This sample was made with 10 per cent. CaO and the fine sand from crushed quartz. It was steamed for 8 hours at 12–15 atmospheres, dried, and then ground as before with a soft pestle in a mortar. The part passing 120 meshes and retained on 200 was retained and subjected to a fractionation process as in the case of the sample just preceding. Four fractions were taken, the analyses of which are shown in the following table:

Table Showing Analysis of Silicate No. XIII.

Fraction number	Per cent. sand	Per cent. combined silica	Per cent. lime	Lime-silica ratio
1.....	55.75	21.75	22.57	1.11/1
2.....	56.70	21.95	21.40	1.04/1
3.....	34.65	32.75	32.60	1.08/1
4.....	1.24	50.00	48.76	1.04/1

Silicate No. XIV.

This sample was made by using three parts of CaO to one of precipitated silica, mixing with enough water to form a slurry, shaking well, and steaming for 8 hours at 15–20 atmospheres. The steamed mass was washed with

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boiled water into a flask and connected to a source of hydrogen sulphide. This gas combined with the lime forming a soluble compound which was washed out. When the lime was removed so completely that there was little action after standing for some time with phenolphthalein, the flask was disconnected and the remaining silicate thoroughly washed. The compound was then dried and fractionated by the use of a heavy solution, as above. Three fractions were taken, the first two being heavy and the last light. The lime-silica ratios were the following:

First fraction (heavy)	1.30/1
Second fraction (heavy)	1.11/1
Third fraction (light)	1.13/1

The following experiments were carried out for the purpose of ascertaining whether there was any more silica rendered soluble by a given amount of lime when the sand from crushed quartz was used than in the case of the Ottawa standard sand. Into each of four platinum crucibles was weighed exactly 0.5 gram of CaO, care being taken to preclude the possibility of any of the same becoming carbonated. Into each of these was then weighed 5 grams of sand, the Ottawa sand being used in two, and that prepared from crushed quartz in the other two. Great care was exercised to keep out carbon dioxide at all stages of the process. The crucibles were steamed for 8 hours at a pressure of 20 atmospheres. One sample from each series was used for the determination of the lime-silica ratio and the other for the determination of the percentage of combined water. The results of this experiment are shown below:

Results of Experiment No. XV.

	Sand from Ottawa standard	Sand from crushed quartz
Lime-silica ratio.....	1.18 : 1	1.15 : 1
Water-silica ratio.....	0.72 : 1	0.76 : 1
Chemical formula.....	$1.2CaO.SiO_2.0.7H_2O$	$1.2CaO.SiO_2.0.8H_2O$

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The results shown in the following table are from an experiment exactly parallel to the one just preceding, except that the amount of lime used was 0.25 gram.

Results of Experiment No. XVI.

	Sand from Ottawa standard	Sand from crushed quartz
Lime-silica ratio.....	1.14 : 1	1.11 : 1
Water-silica ratio.....	0.69 : 1	0.71 : 1
Chemical formula.....		

The results shown in the following table are those from an experiment which differed from the one just preceding only in the fact that the steam pressure was 10 instead of 20 atmospheres:

Results of Experiment No. XVII.

	Sand from Ottawa standard	Sand from crushed quartz
Lime-silica ratio.....	1.09 : 1	1.18 : 1
Water-silica ratio.....	0.90 : 1	1.15 : 1
Chemical formula.....		

Summary of Results of Chemical Analysis.

No.	Composition of mixture (Approx.)	Mols. CaO	Mols. SiO_2	Mols. H_2O	Experiment No.	Pressure in atmospheres
1	$CaO.9SiO_2$	0.86	1	0.63	4	12–15
2	$CaO.19SiO_2$	0.89	1	0.51	5	12–15
3	$CaO.27SiO_2$	0.87	1	0.73	8	12–15
4	$CaO.13SiO_2$	0.84	1	0.84	9	12–15
5	$CaO.27SiO_2$	0.85	1	0.32	10	12–15
6	$CaO.6SiO_2$	0.91	1	0.54	11	12–15
7	$CaO.13SiO_2$	0.84	1	0.75	12	12–15
8	$CaO.9SiO_2$	1.18	1	0.72	15*a*	19–21
9	$CaO.9SiO_2$	1.15	1	0.76	15*b*	19–21
10	$CaO.19SiO_2$	1.14	1	0.69	16*a*	19–21
11	$CaO.19SiO_2$	1.11	1	0.71	16*b*	19–21
12	$CaO.19SiO_2$	1.09	1	0.90	17*a*	9–11

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Summary of Results of Chemical Analysis (*Continued*).

No.	Composition of mixture (Approx.)	Mols. CaO	Mols. SiO_2	Mols. H_2O	Experiment No.	Pressure in atmospheres
13	$CaO.19SiO_2$	1.18	1	1.15	17*b*	9–11
14	$CaO.3SiO_2$	0.90	1	....	2	12–15
15	$CaO.3SiO_2$	0.87	1	....	3	12–15
16	$3CaO.SiO_2$	0.85	1	....	6	12–15
17	$CaO.9SiO_2$	0.82	1	....	7	12–15
18	$CaO.27SiO_2$	0.97	1	....	10*a*	12–15
19	$CaO.6SiO_2$	0.83	1	....	11*a*	12–15
20	$CaO.13SiO_2$	0.89	1	....	12_1	12–15
21	$CaO.13SiO_2$	0.83	1	....	12_2	12–15
22	$CaO.9SiO_2$	1.11	1	....	13_1	12–15
23	$CaO.9SiO_2$	1.04	1	....	13_2	12–15
24	$CaO.9SiO_2$	1.08	1	....	13_3	12–15
25	$CaO.9SiO_2$	1.04	1	....	13_4	12–15
26	$3CaO.SiO_2$	1.30	1	....	14_1	15–20
27	$3CaO.SiO_2$	1.11	1	....	14_2	15–20
28	$3CaO.SiO_2$	1.13	1	....	14_3	15–20

DISCUSSION OF CHEMICAL ANALYSES.

It can readily be seen from the table that the lime-silica ratios are all in the neighborhood of one. This shows that the lime and silica are present in the bonding material of sand-lime brick in nearly equal molecular proportions and that the major part of this bonding material is doubtless the hydrated calcium metasilicate ($CaSiO_3.xH_2O$). The variations from this formula, however, are greater than can be attributed to experimental error, hence there must be other silicates present also. It would seem that with excess of lime, the orthosilicate (Ca_2SiO_4) might be formed, and that with an excess of available silica there would appear a calcium disilicate such as $CaO(SiO_2)_2$. If calcium orthosilicate is formed at all, it would surely appear when lime and precipitated silica are used in the ratio of 3 to 1, as in numbers 16, 26, 27 and 28. But, if they are formed here, why does not the molecular ratio of lime to silica, as determined by analysis,

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show it? In this connection it must be remembered that in an atmosphere of dry saturated steam it is possible that such a compound may be stable, while, when treated with an excess of water, it is very likely broken down by hydrolysis. When excess of silica is used in the mixtures, chemical analysis is difficult, if not impossible, unless the silica be in the form of quartz grains of sufficient size to be only slightly acted on by the dilute alkalies used in the separation. In a mixture composed of such sand grains with 20 per cent. of lime, only the surfaces of the sand grains furnish available silica for the reaction, consequently in the various parts of the mixture the molecular ratio of lime to silica will vary and we would expect several compounds to be formed. Now, if a mixture of compounds such as this be treated with a large excess of water to remove free lime, hydrolysis of the compounds begins, and as the dicalcium silicate hydrates most easily it doubtless goes down to the metasilicate thus:

$$Ca_2SiO_4 + 2H_2O \rightleftharpoons CaH_2SiO_4 + Ca(OH)_2.$$

This is one of the reactions that takes place in the setting of Portland cement, and it is not improbable that even under the conditions here attained, an anhydrous calcium silicate may form which, when treated with water, hydrolyzes as shown in the above equation. In practically all of the samples showing lime-silica ratios lower than one, the samples were washed with a considerable quantity of water, and in some cases a very little dilute acid or hydrogen sulphide gas. In samples 9–13 this was not done, but tests for free lime were made on the material just as it came from the steam cylinder. Trials were made in which the samples would not color phenolphthalein at once but would do so on standing for some time. This appears to be good evidence that the materials hydrolyze, or at least that some of them do.

The conclusion seems to be justified that the ratio in which lime and available silica are present in the mixture

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will determine to some extent the ratio of lime to silica in the molecule formed. Since this varies in different parts of a sand-lime brick mixture, it must be true that there are a number of silicates present in the bonding material, the greater part of which is doubtless the hydrated metasilicate with some orthosilicate and some disilicate.

The water found in combination was quite variable. In these determinations the samples were dried to constant weight at 100° and ignited in the blast furnace. The water in combination was found to vary from about a third of a molecule to something more than a molecule, per molecule of silica. It is evidently held with very different degrees of tenacity and it is quite probable that the amount of water which may be in combination is not a constant.

The amount of water held in combination appears to decrease with increasing steam pressures as shown in experiments 15–17. This must be taken to mean that the decomposition pressure of some hydrate in the mixture is greater at the higher temperatures employed than the pressure of saturated steam, consequently there is a loss of water at the higher temperatures.

From the facts at hand, the conclusion appears to be justified that in sand-lime brick made from pure calcium lime and silica sand we have a mass of sand grains held together by a bonding material which is a mixture of hydrated calcium silicates. The molecular ratio in which lime and silica occur is nearly equal to unity, consequently, the major portion of this material is doubtless the metasilicate of calcium, hydrated to a greater or less extent. Silicates, having a higher and lower lime-silica ratio than one, must also be present to account for the variation in this ratio as determined by analysis. The amount of water in combination is evidently quite a variable quantity.

It must be true that under the influence of steam lime is able to attack silica somewhat as follows:

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$$Ca(OH)_2 + SiO_2 \rightleftarrows CaSiO_3 + H_2O \text{ (or } CaSiO_3.H_2O)$$
$$CaSiO_3 + Ca(OH)_2 \rightleftarrows Ca_2SiO_4 + H_2O.$$

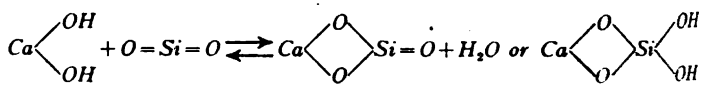
Now, the orthosilicate will doubtless hydrolyze to some extent, as shown in the following equation:

$$Ca_2SiO_4 + 2H_2O \rightleftarrows CaH_2SiO_4 + Ca(OH_2).$$

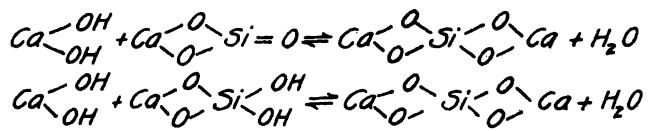
One molecule of lime may also attack two of silica with the formation of hydrated disilicate, thus:

$$Ca(OH)_2 + 2SiO_2 \rightleftarrows CaH_2Si_2O_6.$$

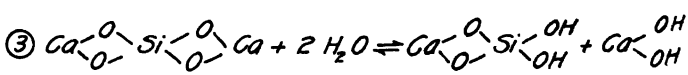
In the light of their structural relations, these reactions appear as follows:

① 

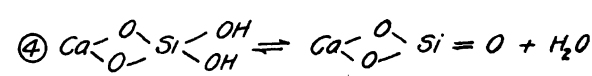
Then again:

② 

and by hydrolysis:

③ 

Water may now be eliminated from this to regenerate the anhydrous compound thus:

④ 

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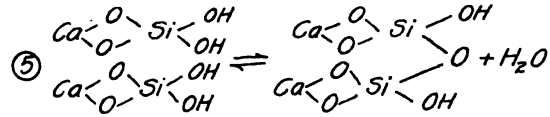
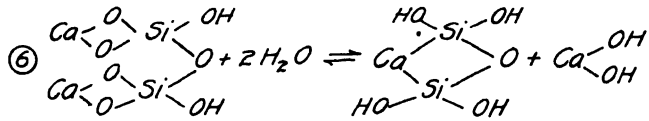
or two molecules may lose a molecule of water between them, thus giving a double molecule with half the amount of water:



Now if this double molecule should lose one of its calcium atoms by hydrolysis, a disilicate would result thus:



It is quite probable that all of these reactions take place at least to some extent. The most stable molecules are doubtless the simplest ones, consequently we would expect to find the mass of silicates composed largely of the simple calcium hydro-metasilicate, and that this is doubtless the case is shown by the fact that the ratio of combined lime and silica is nearly unity. Varying the ratio of lime to available silica in the raw mixture will have an effect on the relative proportions in which the compounds are formed, as does also a variation in the steam pressure on the relative amounts of water held in combination.

PETROGRAPHIC WORK.

By the aid of the polarizing microscope it is possible from considerations based on the properties of light alone, to distinguish between isotropic and anisotropic media. This may be done for substances very finely divided. Thus it would be an easy matter to distinguish between ground glass and ground quartz, or powdered salt and powdered sugar. If the particles are large enough to cover a considerable portion of the field of the microscope, one may

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distinguish further between uniaxial and biaxial crystals or crystalline substances by looking for the interference figures in converging light. This would enable one to say whether the substance crystallizes in either the hexagonal or tetragonal system, on the one hand, or the orthorhombic, monoclinic or triclinic, on the other. If the material occurs in particles large enough, it is possible to do many other things, but for very small particles it is not possible to say more than that a substance is isotropic or anisotropic, unless definite crystals appear.

In order to study this problem, sections were prepared from several kinds of commercial sand-lime brick, of a small sand-lime block made in the laboratory, and of small blocks made from pure silica and lime. Slides were also prepared from material made by heating for about a week, in sealed tubes, mixtures of lime and silica, under a pressure of 120 pounds per sq. in., and in various other ways.

The photomicrographs of sand-lime brick sections shown below (Figs. 1 and 2) were taken by transmitted light without the use of the upper nicol. They show that the bonding material of sand-lime brick is not transparent as are the quartz grains and, consequently, that if crystalline at all the crystals are very small and closely packed.

Figs. 3 and 4 are photomicrographs of a section prepared from equal molecular quantities of pure lime and precipitated silica. The material was thoroughly mixed by grinding in a mortar and, after moistening, subjected to very great pressure in molding. Two small cylinders 0.5 in. in diameter were made, which were steamed in the usual way. The fracture of this material was conchoidal and the luster was vitreous. The sections were made as thin as was consistent with the nature of the material. When examined between crossed nicols, the field was uniformly dark except for small spots in Fig. 3. When examined in plain polarized light without the use of the upper nicol and at a magnification of 315 diameters, such structures as are shown in Fig. 4 were visi-

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ble. The lighter areas are isotropic and evidently must be crystals belonging to the isometric system. The light points which appear between crossed nicols (see Fig. 3) are small crystals which are doubly refracting. It was not possible to make further determinations of these doubly refracting crystals because of their small size.

Larger particles of this doubly refracting compound were found in the material prepared as described under silicate No. XIV, wherein precipitated silica and lime

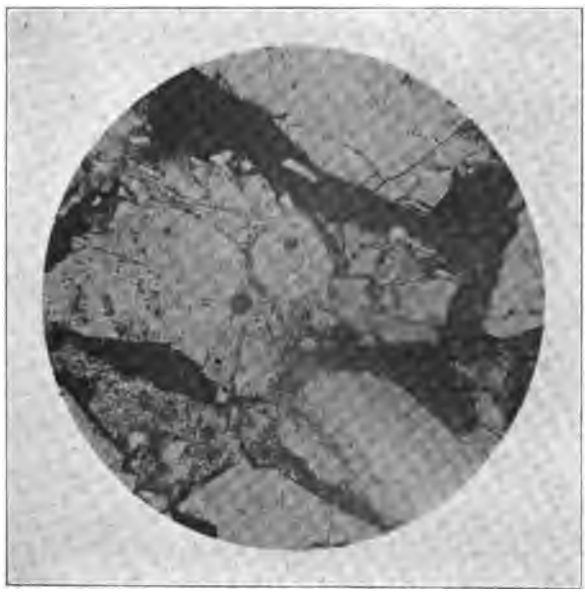

Fig. 1.

were used. Some of this material, after freeing from uncombined lime and washing thoroughly, was put into a hard glass tube and sealed. This tube was then left in the steam bath for about two weeks. The material was then removed, washed and dried. Some of the powder was then mounted in Canada balsam for study. Somewhat larger crystalline bodies were apparent, but nothing

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showing a regular outline that would permit of the identification of the crystal system. This slide also furnished particles which in converged light gave the uniaxial interference figure. Calcium hydrate crystallizes in the hexagonal system and so does calcium carbonate, but under the conditions whereby this material was prepared there is hardly a possibility that enough of either of these compounds could be present to form crystals of such size.

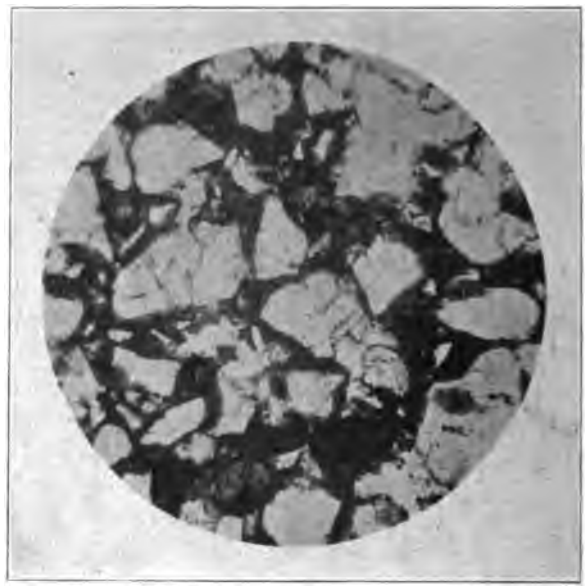

Fig. 2.

It would seem that from microscopic evidence we are warranted in saying that at least two distinct crystalline compounds are present in calcium silicates formed at steam temperatures. The isotropic crystals doubtless represent a compound occurring to some extent in the bonding material of sand-lime brick, but present in larger amounts in the compounds made from lime and fine silica as, for example, that from Southern Illinois, or of such a degree

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of fineness that the reaction penetrates throughout the mass. Sections of sand-lime brick, and in fact all the slides examined, show small, highly double refracting crystalline particles which are doubtless the zeolitic minerals observed by other investigators. The fact that these particles show the uniaxial interference figure in converged light places them in either the hexagonal or the tetragonal crystal system.

GENERAL CONCLUSIONS AS TO THE CONSTITUTION OF SAND-LIME BRICK.

1. Sand-lime brick made from pure materials consist of sand grains cemented together by a bonding substance.

2. Aside from the calcium hydrate or carbonate that may be present, this bonding material consists of a mixture of at least two and most likely three calcium silicates, some of which are hydrated.

3. The bulk of this mixture of silicates is calcium metasilicate ($CasiO_3$ or $CaSiO_3.H_2O$).

4. Other silicates which must be present to some extent are calcium orthosilicate and calcium disilicate, the latter of which may contain one or more molecules of water of hydration.

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MELTING-POINT AND DEFORMATION EUTECTICS.

By HOMER F. STALEY, Columbus, O.

One of the most startling results of the application of physical chemistry to silicates has been the absolute divorce effected between melting and fluidity. Formerly, when we said a substance melted, we meant that it became more fluid, and when a substance became more fluid under heat treatment, we said it melted. Now physical chemistry forces us to admit that these statements are not necessarily true. This has been accomplished by giving definite restricted meanings to the words: solid, liquid, melting and solidification. These are defined as follows:

Solid: physically anisotropic, crystalline.

Liquid: physically isotropic, amorphous.

Melting: change from the crystalline to the amorphous state.

Solidification: crystallization.

Luckily we can still use the word fuse in its accustomed meaning of becoming fluid under heat treatment.

According to the above definition, a substance can melt without any increase of fluidity. Such an instance is noted in the oft-quoted case where Day and Allen[1] observed feldspar to lose its crystalline form, *i. e.*, melt, yet remain rigid. In the same way amorphous substances may become more fluid under heat treatment, yet can never melt. They are already melted.

This had led to the consideration of two kinds of eutectics—the melting-point eutectic and the deformation eutectic.

The Melting-Point Eutectic.—The melting-point eutectic mixture of a given set of materials may be defined as that mixture which requires the least temperature to cause the materials to change from the crystalline to the amorphous state. This is the one to which physical chemists ordi-

[1] Day and Allen, "Isomorphism and Thermal Properties of the Feldspars," Amer. Jour. Science, 4th Series, Vol. XIX, p. 93.

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narily refer when they speak of a eutectic mixture. Such eutectics can be accurately located only by measuring the adsorption of heat which accompanies melting, or by observing the change in the optical properties of the materials due to the change of state.

The location of the eutectic point between two minerals has been well summarized by Vogt, as follows:

"Those minerals which have a high melting point and a relatively high latent heat of fusion have a eutectic point so located that it lies closer in composition to the more fusible mineral. If the difference in the melting points is considerable, the eutectic temperature is very close to the fusing point of the more fusible mineral. The eutectic composition of two minerals having about the same melting point is nearly in the middle. The eutectic composition also approaches close to the lower melting component when the latter has a higher, and the more infusible mineral a lower molecular weight."[1]

The influence of the molecular weight of the components is generally slight, since in silicates high melting point and high heat of fusion usually go together. The difference in relative heights of the respective melting points of the components is the dominant factor in determining the location of the eutectic composition.

The Deformation Eutectic.—The second kind of eutectic has been considerably confused with the first. It has not been given a distinctive name, and, for want of a better, we may call it the "deformation eutectic." A deformation eutectic may be defined as that mixture which requires the least heat treatment to cause fluidity sufficient to result in the deformation of the mixture. Such eutectics are the kind located by the use of cones, or any equivalent means of determining incipient fluidity.

For reasons to be explained, it often happens that the "deformation eutectic" corresponds in composition to

[1] In this statement the word "fuse" and its derivatives are used in the sense now more accurately expressed by "melt."

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the melting-point eutectic. Such a case is illustrated in the SiO_2 : $Al_2O_3 2SiO_2$ binary system, corresponding to mixtures of quartz and kaolinite. Seger[1] found that the "deformation eutectic" contained 80.2 per cent. quartz, while Shepard and Rankin[2] found that the melting point-eutectic contained 78.25 per cent. quartz. The two curves are given in Fig. 1.[3]

It will be noted that the deformation curve lies above the melting-point curve. This means that after the mixtures had been heated sufficiently to cause loss of crystalline state, a further increase of heat will be necessary to produce enough fluidity in the cones to result in deformation.

It will also be noticed that the left-hand side of the deformation curve rises rapidly so that the deformation point of SiO_2 is almost as high as that of $Al_2O_3.2SiO_2$, while the left-hand part of the melting point curve is almost flat and the melting-point of SiO_2 is 170° C. lower than the melting-point curve of the $Al_2O_3.2SiO_2$ mixture. In other words, quartz, or rather cristobalite into which quartz inverts between 800° and 1100° C., melts at about cone 27, while it does not begin to fuse, *i. e.*, become fluid, until cone 35. A refractory material does not necessarily have a high melting point, but it must have a high fusing point.

The deformation curve does not necessarily always lie above the melting-point curve. It may coincide with it or even fall below it. All three relations are shown by superimposing Reike's[4] deformation point data on Day

[1] Collected Writings of Seger, Vol. I, p. 545.

[2] Shepard and Rankin, "Binary Systems of Alumina with Silica, Lime and Magnesia." With Optical Study by Wright. Amer. Jour. Science, 4th Series, Vol. XXVIII, p. 293.

[3] The deformation points in degrees of the Seger cones used in plotting the curves are the estimated values.

[4] Sprechsaal, Vol. 40, p. 595.

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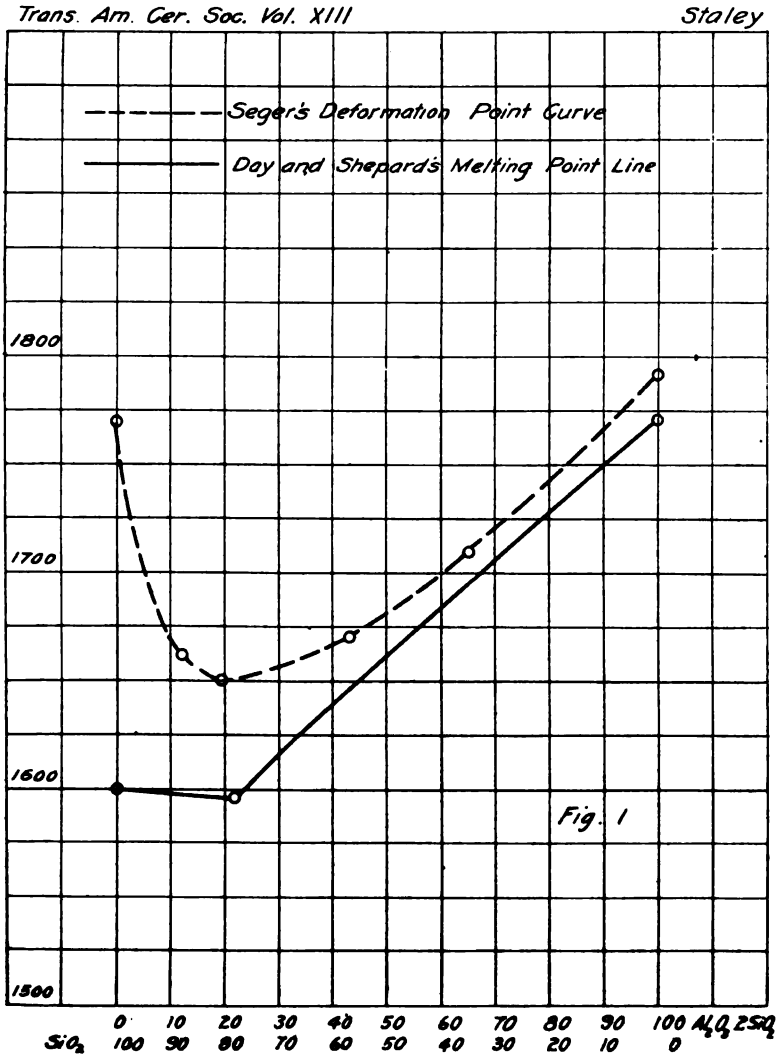

Fig. 1

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and Shepard's[1] melting-point curve[2] for the lime-silica series of minerals[3] (Fig. 2).

The closeness with which the deformation curve follows the melting-point curve depends on three factors:

I. The fluidity of the component materials immediately after melting.

II. The amount of melting-point eutectic present in the various compositions.

III. The height of the melting point of the last of the composition to melt, above that of the eutectic portion.

The effect of these three factors may be summarized as follows:

I. The greater the fluidity of the melted portion, the greater the tendency to deform.

II. The greater the amount of melting-point eutectic present in a mixture, the greater the tendency to deform.

III. The more refractory the excess components as compared with the eutectic, the greater the tendency to deformation before complete melting.

In some cases where the eutectic composition is quite fluid, and its melting point considerably below the melting point of the bulk of the composition, we may have deformation before complete melting of the mixture. In the immediate neighborhood of the eutectic composition, Factor II has great weight, hence the deformation eutectic generally falls in this region. However, the melting point of the last of the composition to melt cannot be high above the eutectic point. So in this region, deformation rarely

[1] Lime Silica Series of Minerals. Day and Shephard, with Optical Study by Wright. Amer. Jour. Sci., IV Series. Vol. XXII, p. 265.

[2] The curve indicates the temperatures at which the last of the compositions melted, *i. e.*, lost their crystalline nature.

[3] The deformation of the $CaO^1/_2SiO_2$ mixture probably took place at a higher temperature than is indicated. Reike's measurements indicate the temperature of the furnace. As this cone was made up of a mixture of SiO_2 and CaO, the heat of combination (28,300 calories), resulting from the formation of $CaO^1/_2SiO_2$ from the oxides, would be liberated at a high temperature and suddenly raise the temperature of the cone much higher than that of its surroundings. We would not expect a compound to deform much before the temperature of complete melting. The fact that CaO enters into silicate combination with a decided evolution of heat is one of the circumstances that makes it a dangerous ingredient in ceramic bodies.

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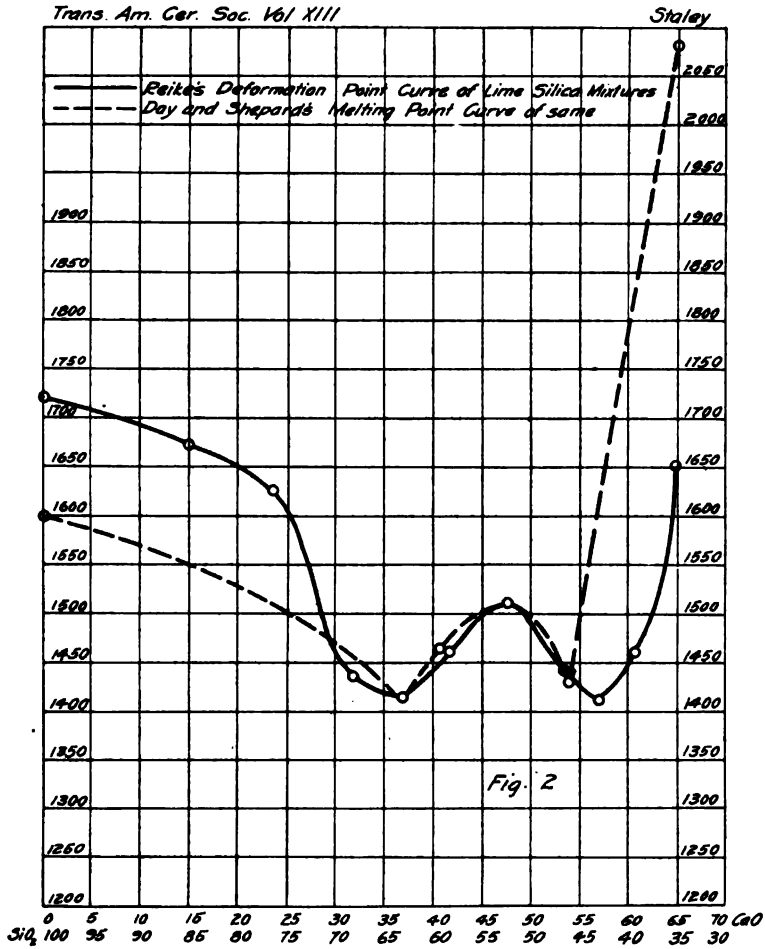

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precedes melting. Of course it would be impossible for the exact eutectic composition to deform before beginning to melt. If the component of dominant effect is but slightly fluid after melting, we may have the deformation curve high above the melting-point curve.

Application of These Principles in the Case of Ceramic Bodies as a Special Case.—Vitrification of ceramic bodies is dependent upon fluidity in the ware. A composition might be entirely melted but not vitrified, or on the other hand, might be vitrified when only a small portion is melted. The vitrification zone of course always lies below the deformation line or zone, and so its upper limit is fixed by the factors that control the position of the deformation zone. The lowest possible limit of vitrification of mixtures of crystalline ingredients is fixed by the temperature at which the eutectic composition begins to melt.

The factors controlling the width of the vitrification zone may be summarized as follows:

I. The greater the fluidity of the melted portion, the more narrow the vitrification zone.

II. The greater the amount of melting-point eutectic present in a mixture, the more narrow the vitrification zone.

We see that for a wide vitrification zone, if one of these factors is large, the other must be small.

The study of the relations between deformation and melting make it plain that deformation-point curves are as valuable, or more valuable, to the ceramist than true melting-point curves. It also warns us of the grave errors into which we may be led if, when applying the results of physical chemical research to our work, we do not distinguish between deformation and melting.

Deformation of Glasses.—All three temperature-composition curves so far given have a minimum at the eutectic composition, and at first thought we might expect the line representing the deformation points of the corresponding frits or glasses to have a minimum at the same place. It is a rather common but erroneous assumption that the

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curve for the softening points of glasses parallels in a general way the melting points and deformation curves of corresponding raw compositions. Eutectic mixtures, however, have little significance in glasses. The softening point line for glasses bears little relation to either the melting-point line or deformation-point line.

It is generally of entirely different shape and its position in regard to the other two lines varies in different cases.

Since glasses are mixtures of liquids, they exemplify the laws for viscosity and fluidity of mixtures of liquids given in the following three cases. Glasses do not conform rigidly to the laws as stated, for these laws apply to homogeneous liquids or mixtures of liquids, and unless prepared with a great deal of care, including several grindings and remeltings, glasses cannot be entirely homogeneous.

Case A.—No chemical compound or molecular aggregation is formed or broken up.

I. The viscosity of mixtures is not quite additive, usually falling a little below what would be expected by the rule of mixtures. Fluidity, the reciprocal of viscosity, is most always additive in liquids.

II. Viscosity decreases at a slowly decreasing rate with increase of temperature. In other words, viscosity is a hyperbolic, while fluidity is practically a linear function of temperature.

III. Each liquid has a characteristic rate of decrease and increase of fluidity.

Case B.—A chemical compound or molecular aggregate (loose compound) is formed. The viscosity curve exhibits a maximum, the fluidity a minimum point.

Case C.—A chemical compound or molecular aggregate is broken down into more simple components. The viscosity curve shows a minimum, the fluidity a maximum point.

According to these, the lines indicating temperature of equal viscosity for various homogeneous mixtures of two liquids in which no chemical action takes place would

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be slightly curved lines approximately parallel to each other. If the two liquids have the same viscosity at given temperatures, the lines of equal viscosity will be horizontal. If not, the lines will be tilted. High and low points on the curve both correspond to compounds. The compositions corresponding to eutectic mixtures fall on intermediate points on the curve and give absolutely no indication of especial fluidity. This is well illustrated by the curve taken from Dr. Schaller's article on Jena glass.[1]

In Fig. 4 we have shown the melting-point line for lead silicates worked out by Cooper, Shaw and Loomis,[2] and the softening point or deformation point line of lead silica glasses[3] given by Mellor, Lattimer and Holdcroft, in Vol. IX, *Transactions of the English Ceramic Society.*

Cause and Effect of Inhomogeneity.—From what has been said up to this point, we might gather that the calculation of the softening point of a glass or enamel is a simple matter. We might be led to say that it would consist of calculating the minerals probably present in it and of knowing the viscosity of these minerals at various temperatures. If this were true, all glasses of the same ultimate composition would have the same softening point. From their experience with empirical formulae, ceramists know this is not the case. The point to the whole matter is that the rules laid down for viscosity of liquids refer to homogeneous liquids, as mentioned, and in glass homogeneity is not readily obtained.

[1] Sprechsaal, Vol. XLII, pp. 614–18.

[2] Am. Chem. Jour., 1909, p. 461.

[3] The part of Mellor, Lattimer and Holdcraft's curve between PbO and $PbO^1/_2SiO_2$ is of doubtful accuracy for two reasons:

(1) As noted by the experimenters, the determination of the softening points actually attempted were distributed by the strong tendency to crystallization in these mixtures.

(2) The authors seem to take it for granted that the softening point of PbO as a glass is the same as its melting point as a crystal. They were probably led to do this by the circumstance that it is practically impossible to keep PbO in the uncrystallized state long enough to determine its softening point as a glass. Since PbO is extremely fluid as soon as melted, this assumption is probably false, and the glass would soften at a much lower temperature than the crystalline form melts. Barring the extremely remote possibility of another compound somewhere between PbO and $PbO^1/_2SiO_2$, the softening points of mixtures of PbO as glass and $PbO^1/_2SiO_2$ as glass should lie on a continuous curve between the softening points of the two ingredients. The sharp break and rapid rise in the curve going from $PbO^1{}_2SiO_2$ to PbO as a glass is extremely questionable.

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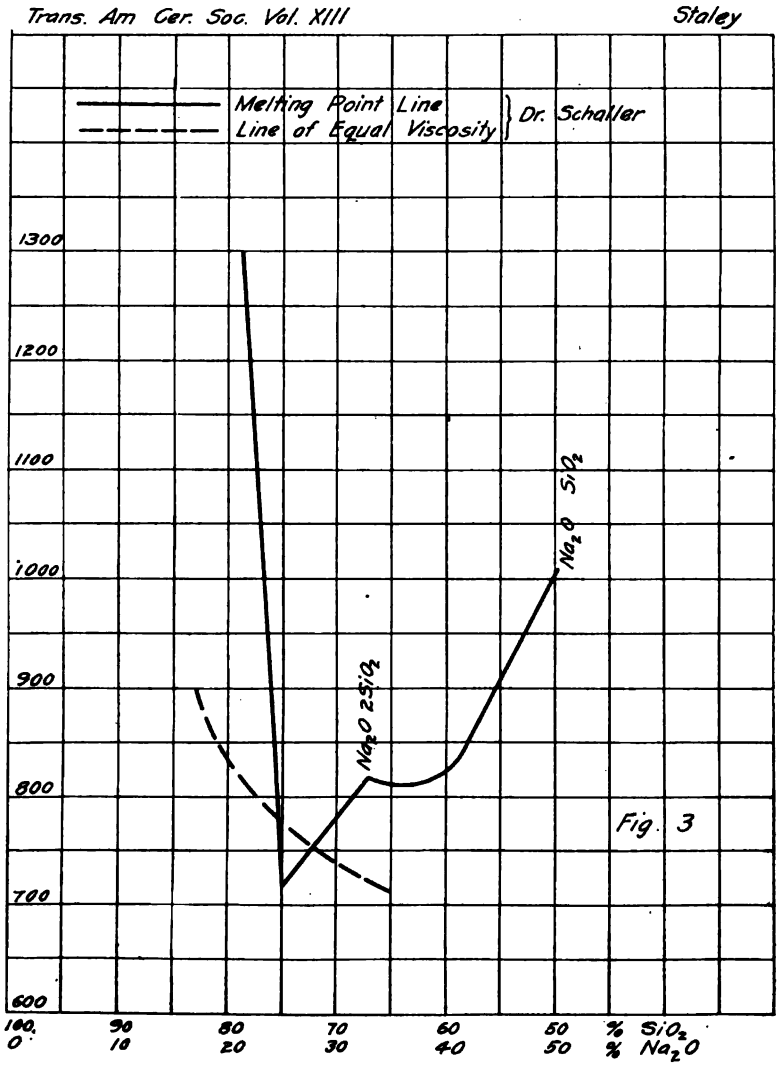

Fig. 3

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The physical and mineralogical condition of the ingredients of a glass both have a decided bearing on the rate of attainment of homogeneity. In the extremely viscous fluids with which we deal, diffusion, or natural mingling of fluids, is very slow indeed. Coarse particles of a mineral of high melting point may remain in the semi-fused glass for a long time before enough material that acts as a flux toward this mineral comes in contact with them to cause them to melt. Moreover, it is perfectly possible for globules of one melted mineral to lie suspended in another for many hours at elevated temperatures. In fact, some cases of opacity seem to be due to this very circumstance. Such mixtures are mineral emulsions. Of course all mineral emulsions are not opaque, this property depending upon the optical characteristics of the liquids. Now the viscosity of a mixture of liquids in the form of an emulsion is not the same as if the mixture were homogeneous. In silicate mixtures it is generally greater.

All glasses pass more or less rapidly through this emulsion state, the degree of homogeneity obtained depending upon:

I. The size of the globules.

This is independent upon the fineness of grinding of the materials used.

II. The rate of diffusion.

This is dependent upon the viscosity of the minerals in the melt, and for each mineral, viscosity is dependent upon the temperature.

III. Time.

For a concrete illustration, we may take SiO_2. If we introduce this in the form of flint, we know that the finer the grinding, *i. e.*, the smaller the globules formed when it fuses, the greater the degree of homogeneity, and, therefore, the less the viscosity of our glass at a given stage in the burn. If we replace fine flint by coarse, and wish our glass to mature in the same time, we must increase the rate of diffusion, *i. e.*, raise the maturing temperature. If we wish it to mature at the same tem-

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perature, we must hold it near the maturing temperature for a longer time. Now if we introduce SiO_2 by means of lime-soda feldspar, a mineral with less viscosity at given temperatures than flint, and so a more rapid rate of diffusion, we know that we may obtain the same degree of maturity if we grind less fine, fire to a lower temperature, or fire for a shorter time. In fact we may make all three of these changes at once.

Since our glass compositions are very viscous and possess a slow rate of diffusion, it is our practice not to allow time for diffusion sufficient to produce a glass at a low temperature. We save time by firing to a higher temperature. The larger the percentage of a mineral which is slow to diffuse, and the coarser it is ground, the higher must we heat the glass in order to develop maturity. The result is that the curve for the maturing point of a given unhomogeneous glass mixture lies above the curve for a homogeneous mixture of the same composition. The greater the superheating necessary, the greater the interval between the two lines.

Raw Glazes.—These are, of course, very unhomogeneous when first fused and must, therefore, be heated to a temperature considerably higher than that at which a homogeneous mixture would develop enough fluidity to be called a matured glaze. When we are dealing with viscous liquids, since time is a factor in diffusion, the compositions that melt first, *i. e.*, those near the eutectic mixture, may be expected to require less superheating than others. On the other hand, many substances and mixtures are very fluid as soon as melted, and in these the line indicating the maturing points for raw glazes practically coincides with the melting-point line. For these reasons the line indicating the maturity points of raw glazes will always lie above the melting-point line and be irregular in shape, for it will be influenced by eutectic relations between the ingredients as well as by the viscosity of these in the melted state.

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WHEN TO FRITT A GIVEN COMPOSITION IN ORDER TO IMPROVE ITS HEAT RANGE.

Body Mixtures.—There is little to be gained by fritting minerals or mixtures which do not vitrify or deform until a considerable temperature interval above the point at which they melt. It will be necessary to heat them up to this temperature whether or not we have destroyed the crystalline form in a previous heating. For instance, there would be little change made by fritting in the vitrification range, or in the final fusion point of quartz or kaolin, or mixtures of these. On the other hand, there is a decided advantage in fritting minerals or mixtures that vitrify and deform before or soon after complete melting. By fritting, we can reduce the temperature at which vitrification sets in, and widen the vitrification zone very materially. In this way, by fritting part of a body composition, it would be possible to convert it from one which fuses suddenly at a high temperature into one which vitrifies gradually at a much lower temperature. Such a method would be especially applicable to compositions containing CaO.

Fritted Glazes.—Any glaze is benefitted somewhat by fritting, as it is made more homogeneous and will, therefore, mature at a lower temperature. The greater advantage, however, comes in those compositions that melt suddenly and immediately become very fluid. By fritting, these can be made to mature gradually and safely at a much lower temperature. As the temperature of volatilization is not lowered by this process, the heat range of the glaze is widened very much. A case in point is the remarkable improvement in the behavior of compositions containing BaO brought about by fritting. It would also be possible to use as fritted glazes many compositions containing lime, which are unworkable as raw glazes.

SUMMARY.

In this article we have attempted the following:

(1) To show the relation between deformation and

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melting, and to call attention to the grave errors into which ceramists may be led if they fail to make this distinction in applying the results of physical-chemical research to their work.

(2) To show the lack of relation between the softening points of glasses and the melting- and deformation-points of corresponding compositions made up of raw materials.

(3) To discuss the cause of unhomogeneity in glasses and glazes and the effect of this in causing glasses of the same ultimate composition (same empirical formula) to vary in viscosity when given the same heat treatment.

(4) To point out the kind of bodies and glazes that will have their heat range lengthened by fritting and those that will not be especially benefitted.

NOTE PREPARED AFTER READING MR. STALEY'S PAPER.

Mr. Kerr: The question Mr. Staley has brought up is of first importance to ceramists and one that will demand more and more consideration as the accumulation of data increases. A definite restriction in the meaning of the various terms used in connection with vitrification phenomena is very much to be desired and the terms used by ceramists should certainly conform with those used by physical chemists. Fortunately, in most of the work that has been done in the field of the silicates, except that done in the Geophysical Laboratory of the Carnegie Institution, the common meaning of melting (*i. e.*, making fluid) has been used. It is equally fortunate that with the great majority of materials, the change from crystalline to amorphous state is coincident with the production of fluidity; hence, the term "melting" is applicable whether used in the old sense of "making fluid" or in the strictly physical chemical sense of "changing from crystalline to amorphous state." There has, therefore, been little or no confusion caused up to the present time.

In the first definition given in the paper the terms "anisotropic" and "crystalline," though used as synonyms, are not synonymous. All uniaxial crystals are isotropic (not anisotropic) but they are nevertheless crystalline, and according to all definitions, they are solid.

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POTASH SALTS FROM FELDSPAR.

By EDWARD HART.

In early times, wood ashes formed the source of potassium compounds; but with the discovery of the Stassfurt salt deposits and the devising of methods for purification of the overlying potassium compounds, potassium chloride and sulfate became and have since remained the source, practically, of all the potassium compounds in common use. While the Stassfurt deposits contain potassium sufficient to supply the world for many years, this forms but a small percentage of the world's total potash deposits, contained in the feldspars and micas of the granite rocks. In this country alone, these exist in tremendous deposits and if the potassium contained in them can be readily and cheaply extracted, it will more than suffice for our own needs, both in agriculture and in the chemical arts.

Up to the present time, however, no method likely to succeed commercially has been devised, although a number of patents have been taken out. The most available material for the purpose of potash extraction would seem to be the refuse obtained in mining feldspar for the use of the potter. This is obtainable in large amount and at low price and should contain, if the feldspar be perfectly pure ($KAlSi_3O_8$), 16.9 per cent. potash.

My experiments on this subject began about three years ago and it soon became evident to me that if commercial success were to be obtained, it would be necessary not only to separate and sell the potassium, but I must also add to this, the pure alumina and the pure silica obtainable from the material, and that these must be as free as possible from iron in order that they might command the highest price.

Several years ago, Jacobs discovered that if barium sulfate be heated in an electric furnace with the proper amount of carbon, barium oxid mixed with sulfide would be obtained. The reactions which occur here are probably as follows:

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$$BaSO_4 + 2C = BaS + 2CO_2;$$
$$BaS + 3BaSO_4 = 4BaO + 4SO_2.$$

It occurred to me that this reaction might be available in transforming the insoluble silicate, feldspar, into a more soluble compound, decomposable by sulfuric acid. My experiments at first were directed to the formation of a barium potassium aluminum silicate by mixing barite and carbon with the feldspar and fusing the mixture, grinding the slag obtained and treating with sulfuric acid. I succeeded in obtaining considerable quantities of alum in this way, but I have since found the best method to be to mix potassium sulfate, feldspar. and carbon in the proportions of 4 molecules feldspar, 4 molecules potassium sulfate and 2 atoms of carbon. It is usually necessary to use rather more than this quantity of carbon to compensate for the formation of some sulfid remaining in the mixture and some carbon monoxid contained in the gas. When perfectly free from sulfid, the glass is light green in color, part of the color being due to traces of iron present. My experiments go to show that the glass is probably more easily decomposed when sulfids are present in some quantity, but I am not quite positive as yet on this point. At any rate, when finely enough ground and treated with diluted sulfuric acid, a residue is obtained, consisting of almost perfectly pure silica and a solution containing alum, potassium sulfate, sodium sulfate from the feldspar and a little sulfate of iron in the form of ferrous sulfate. On evaporating this solution, alum and potassium sulfate crystallize out leaving a mother liquor containing the impurities present in the feldspar and in the reagents, chiefly a little aluminum sulfate, a little potassium sulfate, nearly all of the sodium sulfate and some ferrous sulfate. To this residue, potassium sulfate and a little carbon are added in such proportions as to convert the potassium sulfate on fusion into potash. The potash then unites with the alumina present, forming potassium aluminate. The amount of carbon is so regulated that

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a small quantity of potassium sulfid is also contained in the slag. This being the case, on treating it with water, this slag dissolves, leaving sulfid of iron as an insoluble residue which may be filtered off, the solution containing potassium aluminate. From this potassium aluminate, the alumina is precipitated by passing through it carefully washed furnace gas containing carbon dioxid, leaving in the solution a mixture of potassium and sodium carbonate, which may be crystallized out, purified and sold. The alumina is washed and sold as such. A further amount of alumina may be obtained from the alum by treating it in solution with potassium sulfid. The alumina precipitates in such form that it can be readily filtered and purified for the market, while sulfuretted hydrogen is given off to be converted either into sulfuric acid by the contact process or into sulfur by the Chance-Claus process. In solution we have potassium sulfate, which is separated by evaporation. The products of the operation are then first, silica, which I hope to produce so pure that it may be used by potters and take the place of ground French flint; second, alumina for use in the manufacture of aluminum or aluminum sulfate; third, potassium sulfate, taking the place of the imported article; and, fourth, a small amount of sodium potassium carbonate, useful in the manufacture of soft soaps. Whether the process can be commercially operated will depend, of course, upon the cost of materials, cost of operation of the process and price to be obtained by the products which cannot be predicted with much accuracy for any future period. From present prices, my calculations indicate that the operation can be carried on at a satisfactory profit.

DISCUSSION.

NOTE PREPARED AFTER READING DR. HART'S PAPER.

Mr. Staley: The production, on a commercial basis, of potash from feldspar has long been one of the interesting problems of silicate chemistry. Following are a

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few of the methods that have been proposed. Naturally many of these are based on the J. Lawrence Smith method of decomposition of alkaline silicates.

Methods for fusion of orthoclase with salt or lime separately were patented in England, by Tilghman, 1847; Newton, 1856; and Ward, 1857.[1] More recently, Rodin has developed a process for heating orthoclase with a mixture of salt and lime. In this process, 100 parts of powdered orthoclase are mixed with 53 parts of slaked lime and 40 parts of common salt. This mixture is heated for one hour at 900° C. The powder comes out of the furnace looking much as it went in but it is claimed that 80 per cent. to 90 per cent. of the potash is converted into potassium chloride and can easily be leached out of the fritt.[2] The objection to this process is that it produces a large bulk of by-product which is of little or no value.

Spriller proposed, in 1882, to treat a mixture of orthoclase and fluorspar or cryolite with H_2SO_4.[3] The products to be made were alum, calcium sulfate, finely divided silica and hydrofluosilicic acid. This method was soon shown, by Pemberton, to be too expensive.[4]

Blackmore has taken out a patent for separation of alkali salts from insoluble compounds by means of carbonic acid under pressure.[5]

Cushman and Hubbard have found that fusion or fritting orthoclase with $CaCl_2$ will decompose the feldspar.[6] In the same place these investigators suggest fusion of orthoclase with potash compounds. This is the method proposed by Dr. Hart in the paper now under discussion, but without the use of carbon.

Cushman and Hubbard have published considerable data on the electrolysis of feldspar.[7]

[1] Jour. Soc. Chem. Ind., Vol. XX, p. 440.
[2] Ibid., Vol. XX, p. 439.
[3] Ibid., Vol. I, p. 128.
[4] Chemical News, XLVII, p. 5.
[5] U. S. Patent 772,206. See also Jour. Soc. Chem. Ind., Vol. XXIII, p. 1089.
[6] Jour. Amer. Chem. Soc., Vol. XXX, p. 795.
[7] Trans. Amer. Cer. Soc., Vol. VIII, pp. 180–198. Jour. Amer. Chem. Soc., Vol. XXX, pp. 779–797.

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This later article contains a good discussion of most of the methods proposed for the decomposition of feldspar for the production of potash salts.[1]

They have taken out patents on the electrolysis of feldspar in the presence of hydrofluoric acid. The material is electrolyzed in the anode chamber of diaphragm cells filled with an electrolyte containing hydrofluoric acid. The alkali is neutralized in the cathode chamber by an acid to form a salt.[2] The alumina is also carried to the cathode chamber and can be precipitated. The SiO_2 is left in the anode chamber as hydrated silicic acid. Only about one-tenth the amount of hydrofluoric acid necessary to decompose the feldspar according to stoichiometrical relations is needed. This is because the hydrofluoric acid is regenerated. The advantage claimed for this process is that no large amounts of by-products of little value are produced as the case in fusion methods.

Swaze has obtained a patent[3] on the following method. The feldspar is heated alone until amorphous. It is then heated under pressure with a strong solution of potassium hydroxide. A solution of potassium silicate and aluminate are thus formed. It is proposed to convert these by chemical treatment into potassium hydroxide, alum and fine silica.

Dr. E. Collett, of Kristiania, proposes the following method.[4]

Feldspar is fused with caustic potash, leached with water, and carbonic acid is led into the leachings. The potassium carbonate formed is separated by evaporation and crystallization.

The earthy mass left from the leaching process is treated with the calculated amount of nitric acid, whereby the potassium is converted into nitrate and goes into solution. The residue is treated with sodium bisulfid to dis-

[1] U. S. Dept. Agri., Office Pub. Roads, Bull. 28.
[2] U. S. Patent 851,922. Also Jour. Amer. Chem. Soc., 1907, p. 2040.
[3] U. S. Patent 862,676, 1907. See also Chem. Abst., 1907, p. 3068.
[4] Seventh Internl. Congress of Applied Chem., Sec. II, p. 108.

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solve any iron that may be present, then leached with water. The residue (alumina and silica) is heated, then treated with nitric acid. Alumina only, goes into solution. This is precipitated by ammonia. The products resulting from this treatment are potassium nitrate, alumina and ammonium nitrate.

In this process, no value seems to be attached to the finely divided silica, although it certainly would be as valuable for ceramic purposes as silica recovered from a solution of sulfates.

Mr. Hart: The trouble with the methods cited by Mr. Staley and other methods which have been proposed, but which he has not quoted, and which it is really unnecessary to quote, is that the materials or the operation cost too much money. This is true, for instance, of hydrofluoric acid needed by Cushman and Hubbard and in addition to this, electric current is needed. It is barely possible that Collett's process might be satisfactory notwithstanding the cost of caustic potash, but I doubt very much whether the substances obtained would be pure. In all probability the silica separating would carry both alumina and potash. I am not even sure as yet that my own process, though exceedingly simple and satisfactory when working in the laboratory scale, can be made to work commercially in face of the German competition.

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SOME EFFECTS OF GYPSUM ON CLAY.

By H. E. KRAMM.

Lime may be present in a clay in a variety of forms of which the silicates, carbonates, and sulfates are perhaps the most common.

In the process of breaking down of a rock which gives rise to clay, the greater part of the lime in silicate minerals would probably go towards the formation of calcium carbonates, and these, being fairly soluble, may be leached out and thus may not affect the clay at all.

A smaller part of the lime may find its way into the clay as secondary calcium silicates, such as the micas, or even as primary minerals which have withstood the breaking-down process. At best, the lime carried by these silicates would not be present in appreciable amounts, and the tracing of its effect upon a clay would indeed present a complicated problem.

The behavior of lime when present in a clay as the carbonate, "calcite," is fairly well known.[1] This mineral loses most of its carbon dioxide between 600°–725° C., and the lime thus liberated becomes an active flux, that is, it tends to produce vitrification.

The degree of vitrification, which for all practical purposes may be considered as denoting the fluxing action of the lime, provided there are not other substances present which could act as a flux, can be traced by following the curve of porosity, of a clay-lime mixture which is exposed to a rising temperature. This relation, theoretically, should be an inverse function. A decrease of porosity is caused by the fluxing action of the lime, which, when uniting with the clay substance, forms a fusible magma, and thus, by the filling of pore space or by the breaking down of pore walls, or both, tends to decrease the pore space.

It is reasonable to assume that not all of the lime becomes available at some definite temperature nor even within a small range of temperature, but will cover a considerable range. While some of the lime may become

[1] See R. Rieke, Sprechsaal, 36 and 38, '06; Bleininger and Moore, Trans. A. C. S., Vol. 10, p. 314 (Ed.).

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available, acting as a flux upon the clay and thus tend to decrease porosity, the action of the still escaping gases would be in an opposite direction. Again, since the porosity determination depends upon the amount of water taken up, the vitrified mass, being, as a rule, impervious, may completely surround pore spaces and prevent the entering of the water.

From this it is obvious that porosity curves can only give an indication of the progress of vitrification and it becomes necessary to check, by other means, the results obtained.

This can be done by making use of the specific gravity curve.[1]

Clay bodies lose in density upon vitrification. The variation of specific gravity should, therefore, indicate the degree of vitrification.

This loss, the writer has found, is a small one as a rule and where whole bricks have to be tested, may lie within the range of error in the determination of the specific gravity, especially, if complicated apparatus is not available to make such determinations absolute.

In the following experiments, the percentage loss-temperature curve is used to check the porosity. In mixtures of clay and lime-carbonate or sulfate, there is a considerable amount of volatile matter. The fluctuations in percentage-loss, therefore, cover a considerable range, and a slight error due to manipulation does not cover up results.

The experiments described in this paper were made with the object of determining, if possible, the behavior of lime when in the form of gypsum in a clay. While, as has been said, the action of lime when present in the form of a carbonate is well known, the action of lime in the form of gypsum has not been conclusively explained. It seems to act differently.[2]

The lime, it appears, is liberated at a higher tempera-

[1] See Purdy, Trans. A. C. S., Vol. X, p. 287.
[2] Ries, N. J. Geol. Survey, Vol. VI, p. 63, 1904.

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ture. Experimental data showing just how it behaves, when present in variable amounts, have not been presented up to the present time.[1]

The clay used in the experiments was the white-burning washed china clay from Cornwall, England. Under the microscope it showed, besides the dull white mass of the kaolin, some angular fragments of quartz.

The gypsum was pure alabaster from Hillsboro, New Brunswick. It did not contain anhydrite which is so often found intergrown with gypsum.

Analyses of clay and gypsum, made by the writer in the clay laboratory of Cornell University, gave the results as follows:

	I Per cent.	II Per cent.	III Per cent.
SiO_2	46.46	46.30	.....
Al_2O_3	38.86	39.80	.....
Fe_2O_3	0.58	.....	.....
CaO	none	.....	32.46
MgO	trace	.....	.....
K_2O	1.37	.....	.....
Na_2O	0.63	.....	.....
SO_3	.....	.....	46.50
H_2O	13.41	13.90	20.56
	101.31	100.00	99.52

I. Washed kaolin, Cornwall, England. Analyst, H. E. Kramm.

II. Theoretical kaolin given for comparison.

III. Crystalline gypsum from Hillsboro, New Brunswick. Analyst, H. E. Kramm.

In analyzing the gypsum, the amounts of CaO and H_2O only were determined. The SO_3 was calculated to satisfy the lime.

Two sets of experiments were performed.

[1] See Watts, Trans. A. C. S., Vol. X, p. 267 (Ed.).

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SET I.

The object of these experiments was to determine the effect and behavior of gypsum upon the clay at different temperatures with varying amounts of gypsum.

Mixtures of the two substances were prepared from five per cent. of gypsum up to fifty per cent. differing by five per cent. in each succeeding mixture of gypsum and clay.

Each of these was ground in a ball-mill with water. It was then poured into pans and the water gradually evaporated to a degree which permitted the molding of the mixture into bricks of size 3 : 1 : 3/4 inches.

The bricks were air-dried and divided into sets containing all the mixtures, each mixture being represented in each set by two bricks. After heating for several hours in an air bath at a temperature of about 110° C. to drive off all moisture, the bricks were weighed immediately after cooling.

In placing a set of bricks in the Seger furnace, which was used for the burning, care was taken to have the two bricks containing the same mixture of gypsum and clay at opposite ends of the crucible. If one of the bricks was placed at the bottom, the other was placed at the top so as to neutralize the effects of any variation in temperature within the crucible, and assure uniform results.

The heat was applied gradually for the first half-hour and was then slowly raised to about the heat of the cone to which the bricks were to be burned and left thus for several hours. The heat was finally increased to the melting point of the cone. The gas was turned off at the complete bending over of the cone, the whole operation of burning taking from 4 to 5 hours. The furnace was allowed to cool gradually. As soon as cooled, the bricks were taken out and weighed. The error of weighing throughout the experiment was kept within a range of ten milligrams.

The bricks were partially immersed in water to permit the free escape of the air from their pores. After thus soaking for 24 hours they were covered and allowed to stand for from 2 to 8 days. At the end of this time the

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water was brought to boiling to drive off as much of the air as possible.

The bricks were then weighed first in air, and then suspended in water. From the data obtained the per-centage loss and per cent. porosity were calculated as follows:

$$\text{Percentage loss} = \left(\frac{W_1 - W_2}{W_1}\right) 100$$

$$\text{Per cent. porosity} = \left(\frac{W_3 - W_2}{W_3 - W_4}\right) 100.^1$$

Where
W_1 represents the weight of the unburned brick;
W_2 represents the weight in air of the burned brick;
W_3 is the weight of the burned brick water-soaked;
W_4 is the weight of the burned brick suspended in water.

Different sets of bricks were taken in burning to cones 010, 05, 1 and 3. These sets were reburned to cones 5, 7, 9 and 12 respectively.

The results obtained are given in tabulated form. Each result represents the average value obtained from two bricks which in every case agreed very closely with each other.

For sake of comparison, the results are also shown plotted to scale, some of the porosity curves having been left out, so as to avoid confusion.

Percentage-Loss at Different Temperatures.

Cone	Gypsum 5%	Gypsum 10%	Gypsum 15%	Gypsum 20%	Gypsum 25%	Gypsum 30%	Gypsum 35%	Gypsum 40%	Gypsum 45%	Gypsum 50%
010	13.34	13.79	14.37	14.62	14.79	15.36	16.02	16.22	17.72	18.18
05	14.74	15.89	17.19	17.49	18.58	19.61	19.74	20.59	21.20	20.67
1	15.04	17.15	18.82	20.31	19.63	21.30	21.59	22.75	21.89	22.42
3	15.70	18.24	20.61	23.12	23.37	24.07	25.37	25.19	25.43	23.73
5	15.75	18.52	21.25	23.90	26.28	28.92	30.42	31.50	32.85	31.67
7	15.59	18.38	21.24	23.91	26.10	29.49	32.20	34.97	37.15	39.26
9	15.65	18.45	21.30	24.01	26.57	29.55	32.19	35.27	38.65	39.73
12	Not determined, due to fusion of 50 per cent. mixture.									

[1] See Trans. A. C. S., Vol. IX, p. 211 (Ed.).

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Per cent. Porosity at Different Temperatures.

Cone	Gypsum 5%	Gypsum 10%	Gypsum 15%	Gypsum 20%	Gypsum 25%	Gypsum 30%	Gypsum 35%	Gypsum 40%	Gypsum 45%	Gypsum 50%
010	49.46	48.6	49.17	48.60	48.28	48.02	48.46	48.55	48.50	48.80
05	48.00	46.63	45.05	43.6	41.4	39.7	38.65	37.90	35.67	34.74
1	45.40	43.58	43.20	42.50	39.79	39.32	38.05	39.08	37.18	37.14
3	40.00	39.8	41.2	40.72	40.13	38.52	40.15	39.28	37.9	38.36
5	38.65	39.2	40.40	40.00	41.45	43.10	44.28	45.57	46.14	47.58
7	24.59	25.65	33.99	39.01	42.65	42.15	43.70	43.65	32.08	25.55
9	23.30	24.86	33.69	37.55	39.50	41.02	42.30	42.88	9.93	7.48
12	4.46	2.94	1.97	1.22	26.8	36.6	40.6	30.6	1.94	fused

It is but natural to expect that the percentage loss since it depends upon the loss of SO_3 would be in proportion to the gypsum content of the brick. A glance at the chart (Plate I), however, shows an overlapping of some of the curves, particularly in the case of the mixture containing 50 per cent. of gypsum. In all cases, the losses of the different samples are so close to each other that a slight error of manipulation can account for it; moreover, they tend to straighten out and become regular towards higher temperature points.

A comparison of corresponding points along the two series of curves show interesting results.

The curves start from cone 010, which is equivalent to 950° C. At this temperature, all water is driven off and the volatile matter remaining in bricks consists, therefore, of SO_3. It is seen that the percentage loss is fairly regular, increasing with the gypsum content.

The corresponding temperature point on the porosity curves shows all mixtures to be within a close range of porosity, between 48 per cent. and 50 per cent., although some overlapping of the curves takes place.

A uniform increase of loss up to cone 05 is accompanied by a uniform decrease in porosity. Since this decrease is approximately proportional to the lime sulfate content,

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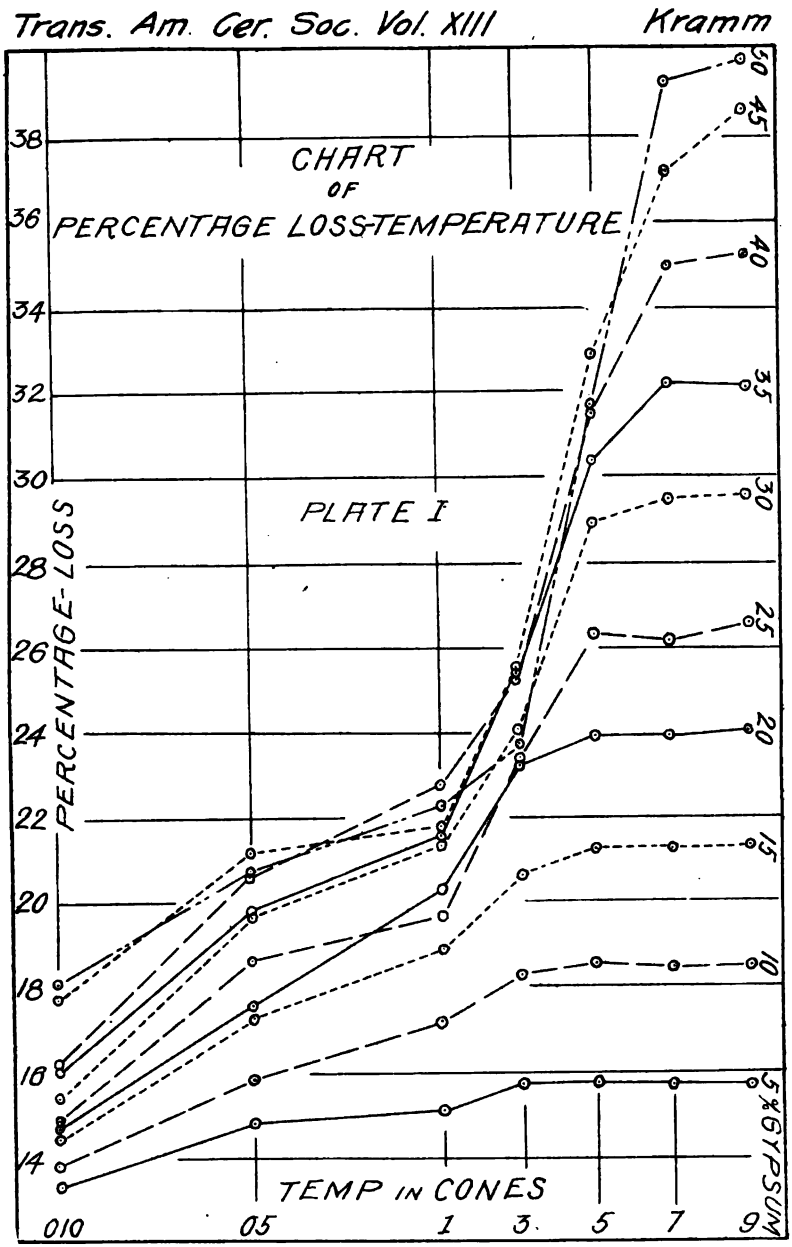

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it means that up to this point the lime, as soon as freed from its SO_3, can act as a flux, causing vitrification.

Between cone 05 and 1, the percentage-loss shows a gradual increase in all the bricks. The corresponding temperature interval of the porosity chart indicates a uniform decrease of porosity in all mixtures, up to 35 per cent. of gypsum. Bricks with greater gypsum content show an increase of porosity.

With the higher percentages, the amount of SO_3 given off is a considerable one. The fluxing action of the lime can not keep pace with the evolution of the gas driven off, hence, greater porosity. This, however, could also be caused by the "blowing-up" effect of the escaping gases.

Between cone 1 and cone 5 the evolution of the gas is a rapid one. All the SO_3 of mixtures, up to 25 per cent. of gypsum, is practically driven off as indicated by the straightening out of the percentage-loss curves. Five and ten per cent. mixtures have lost all SO_3 at cone 3.

The corresponding temperature interval of the porosity chart is marked by a rapid decrease of the curves representing mixtures with low gypsum content.

Bricks containing more than 20 per cent. of gypsum show an increase of porosity which becomes more pronounced as the gypsum content increases.

From cone 5 to cone 9, the changes are less marked in the percentage-loss chart. The bricks with high gypsum content still lose some SO_3, and the tendency of all curves is toward constancy.

The percentage loss at cone 12 could not be determined, due to the fusion of the bricks containing 50 per cent. gypsum and consequent spattering of the fused material onto other bricks.

The porosity curves, on the other hand, show a considerable variation. Practically all of the SO_3 having been driven off, the fluxing action of the lime thus liberated is an active one. It is seen, however, that the decrease of porosity has no relation to the gypsum content. Mixtures contain-

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ing up to 20 per cent. of gypsum show a rapid decrease and at cone 12 are practically vitrified. Mixtures from 25 to 40 per cent. still show a high degree of porosity at cone 12, which increases regularly towards the 40 per cent. gypsum and mixture.

The bricks containing 45 per cent. of gypsum again show a high degree of vitrification, while the 50 per cent. mixtures fused and were completely vitrified.

To sum up: The percentage loss curves show an increase which is approximately proportional to the amount of gypsum the mixtures contain. The rate of evolution of SO_3 is a gradual one at lower temperatures and a pronounced one between cone 1 and 5.

Comparing these results with the behavior of porosity or progress of vitrification, it is seen that the fluxing action of the lime is a variable one. While its progress seems to be fairly regular at lower temperatures, at higher temperatures a quantity of available CaO accumulates which does not affect the porosity curves. This seems to combine suddenly, causing dropping of the porosity curves.

Furthermore the curves indicate one point of minimum fusion, at which the porosity even at cone 12 is quite high, and two points of maximum fusion which are, in all probability, eutectic points.

SET II.

While the foregoing deals with the behavior of the lime at different temperatures, the time of burning of the bricks being approximately the same at each temperature, the question has to be considered as to the effects of prolonged burning, and as to what is the lowest temperature at which it would be possible to drive off the SO_3 and liberate the lime.

To determine this, six sets of nine bricks each were prepared, the percentage of gypsum in them varying from zero to fifty per cent. with 10 per cent. differences between samples. The preparation of the bricks was done in the same manner as before, the size of the bricks being about that

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of inch cubes. The bricks were air-dried and then burned in the Seger-furnace. The temperatures were recorded by means of a thermo-electric pyrometer.

During the first burn, the bricks were kept for 8 hours at 790° C. When placed in water it was found that the mixture had not lost its plasticity, for the bricks slaked down, necessitating the molding of a new set. These were burned at a temperature of 950° C. The furnace was brought to this temperature and kept there for two hours. The test pieces were then removed and the loss in weight determined. The operation was repeated until, at the fifth burn, no more loss of weight occurred.

In determining the porosity after the first burn, the bricks were partially immersed in water. It was found that, after standing, beautiful bundles of selenite crystals had formed on the projecting surfaces of all the gypsum mixtures.

A possible explanation for this seems to be that the alkaline salts, which the analysis shows to be present in the clay, have combined with SO_3 forming alkaline sulfates.

In the heating of the bricks, the tendency of soluble salts would be to travel to the outer portion of the brick, causing "white wash." The water in its passage through the brick, where, no doubt, uncombined CaO existed, dissolved part of it, and the reaction of this water with the alkaline sulfates would give rise to secondary gypsum. The formation of crystals was not observed at any other stage of the burning.

What the chemical nature of the mixtures is after the fifth burn, which showed no more loss (Plate IV), can only be surmised. On the one hand there is the possibility that sulfates have formed which are more stable at higher temperatures. On the other hand, it is possible that the heating effect is not the same in all parts of the brick, being naturally more intense near the surface and less intense towards the center. This difference may be

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sufficient to permit only a portion of the gypsum to be broken up.

The experiment was continued by subjecting the bricks to a higher temperature; two hours' burning at 1110° C., resulting in a small loss of weight, made repetition necessary, until at the end of 40 hours' exposure to this temperature constant weight was obtained. The results of these burnings are shown in the accompanying diagrams (Plates III and IV).

Plate III shows percentage-loss curves with varying time. It is self-explanatory.

The percentage of volatile matter in the bricks, when calculated from the analysis given in the preceding pages, show results as follows:

Per cent. gypsum	Per cent. clay	Per cent. volatile matter	Actual per cent. loss (Plate IV)
0	100	13.41	13.06
10	90	18.83	17.80
20	80	24.24	23.87
30	70	29.66	28.65
40	60	37.07	35.35
50	50	40.48	39.90

Comparing these values with the loss of the percentage-loss curves, it is seen that the loss falls somewhat short. To make sure that all SO_3 was driven off, the bricks were tested for sulfates by the silver-coin test, which failed to show traces of it. The error, which is only a slight one, lies, therefore, with the analyses.

Plate IV shows, for comparison, the curves of porosity and percentage-loss of volume varying with time. They supplement each other. As the loss increases, the porosity increases and *vice versa*. Comparing the porosity curves with the curves of Plate III, it is again demonstrated that the fluxing action of the lime is an irregular one. With a fairly uniform and slow rate of loss and with constant temperature the loss is not always accompanied by a decrease of porosity.

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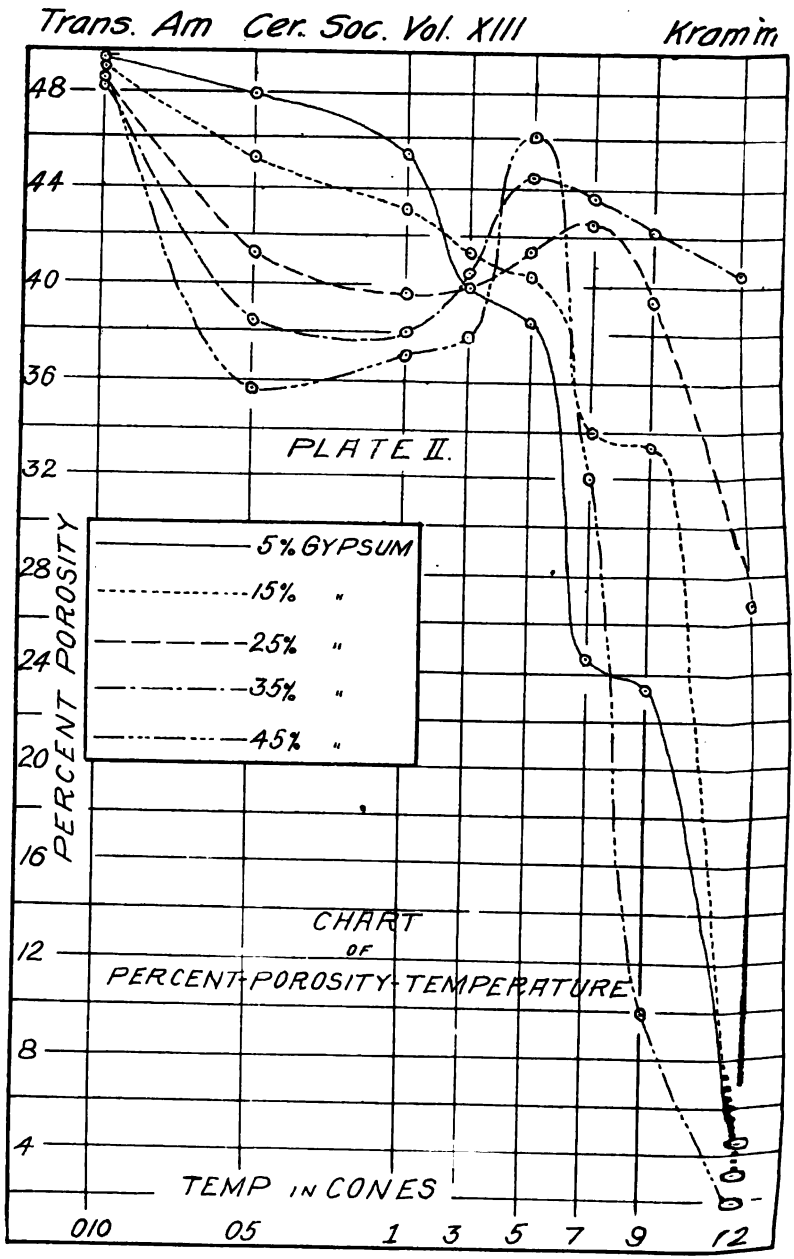

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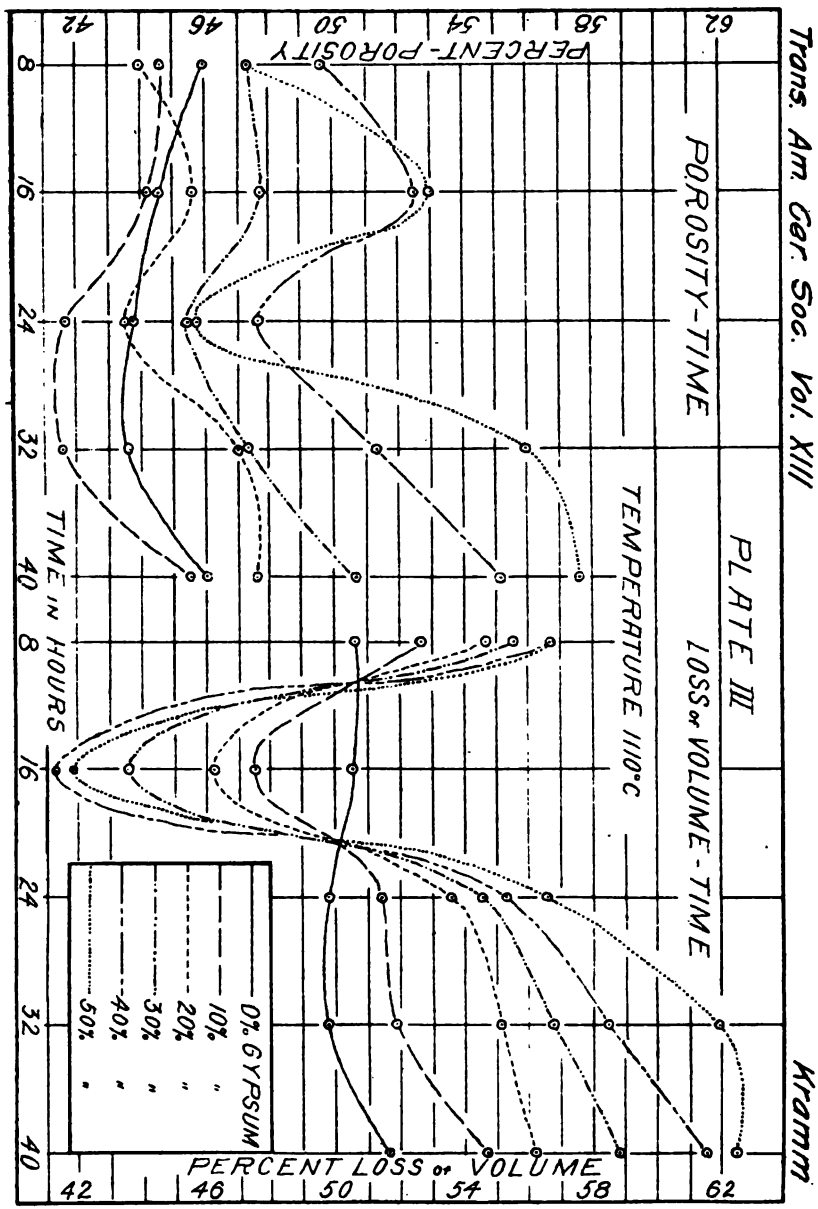

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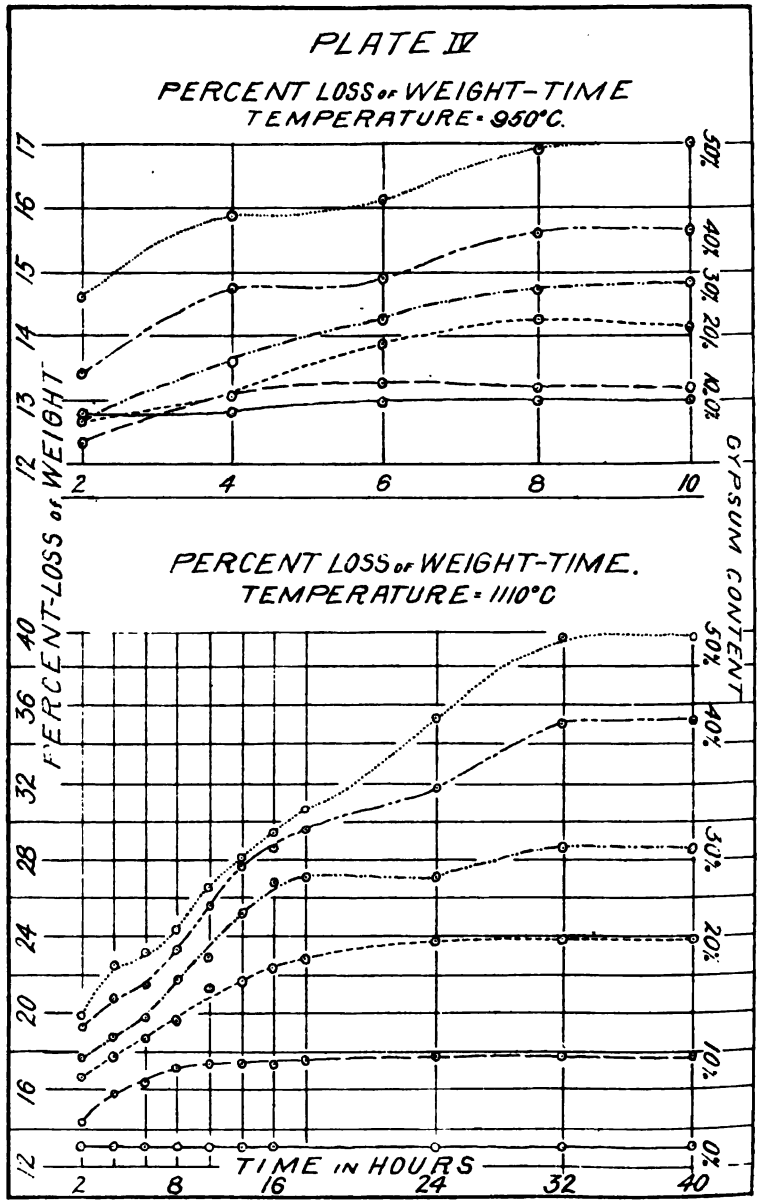

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CONCLUSIONS.

In the preceding pages, the facts demonstrated are the following:

(1) The gypsum-clay mixtures retain their plasticity to a temperature higher than was expected. In this case they were still plastic after 8 hours' burning at 790° C.

(2) The SO_3 of the gypsum is driven off gradually at temperatures up to cone 1. Beyond this point the evolution of gas is very rapid and probably causes "blowing up," at least it suddenly increases the porosity.

(3) All the SO_3 of the gypsum may be driven off at a temperature of about 1100° C. The evolution of gas being slow at this temperature, the "driving off," therefore, depends entirely upon the time of burning. It has also been shown that at 950° C. it is not possible to drive off all SO_3. This may be due to the formation of chemical compounds which have a greater temperature resistance, or to unequal heating effects, the temperature towards the center of the brick being lower than that near the surface.

(4) The lime when liberated acts as a flux but its fluxing action is eccentric. A comparison of the porosity and per cent.-loss curves shows that, at certain stages of the burn, a quantity of lime accumulates which does not affect the porosity curve until a certain point is reached; it then suddenly combines, causing vitrification.

(5) The range of mixtures of gypsum and clay experimented with exhibit at high temperatures one point of minimum fusion and two points of maximum fusion. The latter are probably eutectic points.

The writer, in closing, wishes to express his obligation to Dr. Heinrich Ries, of Cornell University, under whose direction the experimental work was performed.

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NOTE ON "VITRIFICATION RANGE AND DIELECTRIC BEHAVIOR OF SOME PORCELAINS."

By J. MINNEMAN, Barberton, O.

A paper with this title, written by Bleininger and Stull,[1] was greeted with considerable interest by electrical porcelain manufacturers, but unfortunately, the data on dielectric strength which they gave has proven of little value owing to the fact that the most important factor, the length of time of testing, was not considered, or at least it was not mentioned.

It has been found that a given piece of porcelain will stand a high voltage for a few seconds, but will be punctured when subjected to a much lower voltage for a number of minutes.

Recently, the writer tested a number of pieces of porcelain, under oil, bringing up the voltage as quickly as possible to the puncturing point. Then a number of similar pieces from the same lot were punctured, bringing up the voltage at the rate of 20 k.v. per minute, until the puncturing point was reached (about 70,000 volts). Upon comparing the results it was found that the pieces which punctured after a rapid increase of the voltage had stood a 25 per cent. higher voltage per mm. before puncturing than had those pieces which had been subjected to a lower voltage for a longer period of time.

This fact is daily verified in every high voltage porcelain plant. In the routine commercial tests, each type of insulator is tested to a given voltage for a given length of time. For example, 100 pieces will be placed on the testing rack and tested for a total time of five minutes; immediately, one or two pieces may puncture, owing to cracks or flaws, but others will stand up for several minutes and then puncture: often pieces are seen to puncture just before the test is completed, having stood the voltage for

[1] Trans. A. C. S., Vol. XII, p. 628.

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almost five minutes before going down. It is owing to this that an exceedingly high factor of safety must be used in testing.

What the action or nature of this "fatigue" may be is not definitely known, but would bear some investigation.

It is evident, however, that results, not based on the average of a large number of pieces or in which no consideration of this time factor is taken, will be of little value. This may account for the wide disparity of the "puncture volts per mm." obtained by Messrs. Bleininger and Stull. Even though the tests were made in approximately the same length of time, it is impossible for any other investigator to check such results, not knowing this time.

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KILN FLUE REGULATION ACCORDING TO SOME VENTILATION FORMULAE.

By DWIGHT T. FARNHAM, Seattle, Wash.

There are humberless rules of thumb by means of which kiln builders regulate the size and number of the secondary flues in a kiln bottom. These run anywhere from the practical formula of an old mason who, while putting in a circle flue in a sewer pipe kiln was asked how he told how big to make the openings left in the top of this flue, replied that he made each one a little smaller as he went toward the stack, and if the last one was so small he couldn't see it, he went back and "chipped each one out a bit," to the kiln burner's rule of building every flue with twice the area of all the flues that emptied into it. This last has its good points until you come to the stack which is likely to be a monstrosity. The mason had the right idea too, but both rules are rather vague and are likely to develop peculiarities when applied in certain cases.

In this discussion the writer intends to keep strictly away from kilns whose interior draft is regulated by means of innumerable exterior dampers. This includes all sorts of kilns with multiple stacks located on the walls or on the crowns and all kilns whose main flue to the stack is divided into several parts, each one of which draws from a limited floor section, and is regulated by a separate damper. Very fine results can be obtained from such kilns, but with a clay whose vitrification range is narrow and where you are burning about six hours ahead of your settle it requires extraordinary intelligence on the part of the burners to handle the large number of dampers to the best advantage.[1]

[1] A case of this sort would be as follows: If a section is "high" at 6 A.M., you fire it heavy until 9 A.M., then fire lighter until noon when that section evens up with the rest of the kiln; whereas, if you had continued to fire heavy until noon, the section would have kept on settling, would have been ahead of the rest, and you could have kept up the see-saw indefinitely.

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The type of kiln we are considering is designed with the idea of being automatic in its regulation; that is, once it is regulated so that it burns evenly when judicially fired and the ware in all parts of the kiln settles evenly, it can be left alone as far as regulation is concerned. The regulation in this type of kiln is done after the kiln is burned off, and should be easily effected. The head burner can himself then make any slight change in the secondary flue openings which he deems necessary after inspecting the burned ware. On a large yard where there are a million and a half brick burning at a time, he can more efficiently regulate the kilns at this time. Under these circumstances, efficient regulation would be a problem did it have to be attended to during the burn. Kiln regulation is a delicate matter and should be under the supervision of a man of high intelligence. The more the work can be concentrated the better will be the results.

DESCRIPTION OF THE KILN TO BE REGULATED.

The kiln we have under consideration is a kiln used to burn paving brick. The inside length is 148 feet, the width between flash walls 16 feet, giving a total floor area of 2,368 square feet. The details of construction necessary to an adequate understanding of the following subject matter are shown in the accompanying photographs. The main flue which extends through the center of the kiln from end to end is 36 inches wide and 36 inches to the spring of the crown which has a rise of 10 inches. This is equivalent to a rectangle 36 x 41 inches and has an area of 1,584 square inches. Outside the kiln wall, this main flue empties into larger flues which lead to the large stacks, 4 x 4 feet inside, located at either end of the kiln. Midway of the kiln and built upon its hub are two small stacks, 2 x 2 feet inside, at whose bases are located flues of equal size leading from the main flue. Opening into the main flue are 248 secondary flues which are merely the spaces left between the feather walls. The openings from between these walls into the main flue were originally 5

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inches by 16.5 inches. On top of these feather walls are laid the floor brick—in this case pavers held an inch apart by wads of clay so that each opening is 1 x 5 inches. There were originally 2,850 of these openings in the floor of the kiln. Nine of these kilns are being operated at the present time and a tenth is in the course of construction.

They have a holding capacity of 300,000 standard paving brick and a daily output of 11,500 brick each.

Plate I.—Excavation about half finished.

As stated before, all the secondary flue openings were 16.5 by 5 inches. Some effort had been made to offset the harder pull near the large stacks by more or less empirically blocking off sections of the floor near the doors, otherwise the burners relied upon the handling of the damper and the method of firing for control.

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The writer had been making some study of the behavior of air in ducts in connection with a drier and it seemed as if the laws so carefully worked out by the Ventilation and Blower Engineers might be employed to advantage in regulating the ducts in a kiln bottom. A number of these laws were discussed briefly last year in a paper on "Dryer Engineering." These laws are taken up in detail in Carpenter's "Heating and Ventilation of Buildings." This book also contains a good equalization table and a diagram showing the dimensions of circular pipes equivalent in capacity to various rectangular pipes. Both of these tables are time savers.

REGULATION FORMULAE.

The formulae applied to the problem in kiln flue regulation under discussion were as follows:

$$\text{I.} \quad d = \sqrt[5]{\frac{32\,a^3b^3}{\pi^2(a+b)}}$$

To find the diameter of a round pipe d which shall be equivalent in carrying capacity to a rectangular pipe with dimensions a and b:

$$\text{II.} \quad N = \left(\frac{D}{d}\right)^{5/2}$$

D = Diameter large pipe or main
d = Diameter small pipe or branches
N = Number of small pipe which will take air from large pipe to best advantage.

$$\text{III.} \quad R. \text{ varies as } 2(a+b) \times 1.$$

The resistance varies as the extent of the rubbing surface or the perimeter of the airway multiplied by its length.

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APPLICATION OF THE FORMULAE.

The first formula is used to reduce the various square flues to their equivalent circles. The second is used to find out how many secondary flues the main flue will take care of—or how many floor openings, as the case may be. The third is used in a general way to illustrate the necessity of having the secondary flue openings smaller as the stack is approached. As the length of the main flue to be traversed diminishes, the perimeters of the openings from the secondary flues must diminish in order to offset the decrease in 1.

Plate II.—Wheel scraper used in excavation.

The writer wishes to state that these laws, especially the last one, are applied roughly, as certain obvious constructional difficulties and practical considerations make an exact application inadvisable.

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Looking at view 8, it will be observed that each kiln has four stacks—a large one at each end into which the ends of the main flue empty, a small one on each side connected with the main flue by short flues at right angles to it. Each large stack is four feet square inside. Each small stack is two feet square inside. For convenience, we will consider one-half the kiln bottom at a time, drawing our line at right angles to the main flue in

Plate III.—Foundation nearly completed, shows location of main flue.

such a manner as to bisect the small stacks. This gives us a main flue 74 feet long having a stack four feet square at one end, and one half of two stacks, each two feet square, or the equivalent of one stack two feet square at the other.

APPORTIONING THE MAIN FLUE.

It is evident that the large stack, if of the same height as the small stack, will take care of more than half of the

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main flue. The proportion of the main flue which should be tributary to each stack is found as follows:

Large stack diameter is 4 feet or 48 inches which is equal in carrying capacity to a circle whose diameter is 54 inches (see Formula I or use Carpenter's Equivalent Curve).

Small stack diameter is 2 feet or 24 inches which is equal in carrying capacity to a circle whose diameter is 26 inches (as above).

Plate IV.—Main flue complete, showing openings into secondary flues.

Turning to our Equalization Table or by applying Formula II, we find that a circular main whose diameter is 54 inches will equal in carrying capacity 6.2 circular branches whose diameter is 26 inches. In other words, our ratio is 1 to 6 and the large stack will take care of five-sixths of the main flue and the small stacks will take care of one-sixth.

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NOTE.—Calculations of this sort are very often based on the relative areas of ducts to be compared. This is incorrect. Areas are not used in the above nor in the computations to follow. If we had used areas in the above our calculation would have been as follows:-

Plate V.—Main flue, feather wall partly in place.

Area large stack, 16 square feet.

Area small stack, 4 square feet.

16 divided by 4 gives a ratio of 1 to 4, which misses the truth by about fifty per cent.

DETERMINATION OF THE NUMBER OF SECONDARY FLUE OPENINGS.

In the half-kiln bottom which we are considering there are sixty-two openings between the feather walls shown in views 6 and 7 which we will call secondary flues. The opening from these flues into the main flue are shown

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in view 4 and there are 64 of them on each side of the main flue in the half kiln. Therefore, using our ratio as determined above we find that 5/6, or 52, of these secondary flues are tributary to the large stack, and 1/6, or 10 of them, are tributary to the small stacks.

DETERMINATION OF THE SIZES OF THE SECONDARY FLUE OPENINGS.

Having determined the number of openings which the large stack should take care of, it now becomes necessary to determine the size of these openings. Formula III tells

Plate VI.—View of feather walls and the secondary flues between them.

us that the "Resistance varies as the extent of the rubbing surface, or the perimeter of the air-way, multiplied by its *length*." The main flue is the same size throughout its length so we may consider its perimeter constant. The *length*, however, varies; that is, the gases have to traverse

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to a greater or less degree the length of the main flue, in proportion to the opening's remoteness from, or nearness to, the stack. Gases from a furnace close to the stack pass downward through the ware, through the floor openings in the secondary flues and then through the main flue openings into the main flue, having only a small portion of the main flue to traverse before reaching the stack. If the gases are generated in a furnace fifty feet away they encounter the same resistance *until* they reach the

Plate VII.—Feather walls complete ready for the floor brick.

main flue. Then they have to travel fifty feet further, all the while being retarded by the friction of the walls of the main flue.

It is clear that some arrangement must be made to offset this if an equal pull from each furnace and an equal burn or equal settle on the part of the ware in all parts of the kiln is to be obtained.

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The method adopted by the writer was that of varying the size of the openings into the main flue, increasing their size as they became more remote from the stack.

In this way a small quantity of air under a comparatively high pressure is admitted to the main flue close to the stack where the pull (unreduced by the frictional resistance of the main duct) is greatest and a larger quantity of air at a comparatively low pressure is admitted to the

Plate VIII.—Kiln complete—150 feet long—holds 300,000 paving brick.

flue fifty feet or so away from the stack where the pull is less. In this way, the number of cubic feet of air or gas per minute (the area times the velocity) entering the main flue through the openings throughout its length is the same, and the cubic feet of air, or gas, per minute passing downward through each portion of the kiln is the same. This tends to make an even burn more easily

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obtainable. Also the quantity (cubic feet per minute) of air being drawn through each grate is uniform. This is very essential when there are fifty fire-holes on each side of a kiln.

Theoretically, each opening into the main flue should be slightly larger than the previous one, increasing in proportion to its remoteness from the stack. This would be difficult if not impractical from a constructional standpoint, however.

THE PRACTICAL APPLICATION.

View 4 shows the main flue in process of construction. The feather walls have not been put in and the openings are seen as originally constructed, being the width of a brick by the thickness of six brick or 5 inches by 16.5 inches. When it became evident that these openings should be decreased as they approached the stack it was found easiest, from a constructional standpoint, to block off each hole by placing two or three brick across the top of the opening, cutting notches in the supporting piers to take the ends of the brick.

To exactly graduate the openings it would have been necessary to cut the brick, so inserted, a different thickness for each hole. We felt that such exactness would amount to rather expensive hairsplitting so the openings were graduated by groups, one brick being inserted in the top of, say ten openings, two bricks in the next and so on. This method was found to be exact enough for all practical purposes.

Inasmuch as we have determined that the size of the openings should gradually increase as they become more remote from the stack, we have now to determine just how large each opening or group of openings shall be. It is evident that the sum of the carrying power of all the openings should equal the carrying power of the main flue.

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CALCULATIONS.

Here is a case for the application of Formula II. The main flue is equivalent to a rectangle 36 x 41 inches. Putting this through Formula I, we find the main flue is equal to a circle whose diameter is 42.298 inches.

The width of all the openings into the main flue is 5 inches. We call this "*a*" in Formula II. "*b*" is the other dimension of the opening. If the opening, as shown in view 4, is all closed up except one brick, we have what we will term, for convenience sake, "one brick out," or an opening into the main flue 5 inches by 2.75 inches. This represents "*b*" in this particular case.

"Two brick out" gives us an opening 5 x 5.5 inches, three brick 5 x 8 inches, four brick 5 x 11 inches, five brick 5 x 14 inches and six brick out an opening 5 x 16 inches.

If "*a*" is 5 inches and "*b*" is 2.75 inches, the openings we find (by Formula I) are equal in carrying power to a circular opening having a diameter of 4.048 inches. Using Formula II, we find that the main flue (D = 42.298 inches) will equal in carrying power 352.84 such openings. Each one of these openings represents, furthermore, 0.28 per cent. of the carrying capacity of the main flue (1 divided by 352.8).

Each opening, "two brick out," "three brick out," etc., is considered in the same manner which results in the following table:

Size of opening	*b* dimensions	Diameter of equivalent circle or "*d*"	Number of openings of this size main flue will take, or N	Percentage each one is of the whole
"One brick out"	2.75″	4.048″	352.84	0.28
"Two brick out"	5.5″	5.774″	145.20	0.69
"Three brick out"	8.0″	6.928″	92.10	1.08
"Four brick out"	11.0″	8.045″	63.37	1.58
"Five brick out"	14.0″	8.984″	48.10	2.08
"Six brick out"	16.5″	9.673″	39.987	2.50

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In figuring any kiln, it is necessary to work out a similar table based on the size of the main flue in question.

Having determined how many holes of any size the main flue will properly take, it becomes necessary to determine how many of *each* size we shall have in order to graduate the holes properly as they approach the stack. In other words, we must determine what combination of holes will give us our necessary graduation and still allow the sum of the percentages to equal 100 per cent., or the carrying capacity of the main flue. This is necessarily—for constructional reasons—a more or less arbitrary selection. In this particular case the following selection was made:

Openings into Portion of Main Flue Tributary to Large Stack.

Number of openings one side of flue	Number of openings both sides of flue	Number of "brick out"	Percentage of openings
2	4	6	10.0
3	6	2	4.14
4	8	3	8.64
5	10	4	15.80
6	12	5	24.96
6	12	6	30.00
—	—	—	—
Total 26	52		93.00

It will be observed that only half the number of holes previously mentioned in the description of this kiln are left open. In order to bring the total percentage under 100 per cent. and still graduate properly, it was found necessary to block off every other opening. Theoretically, this is correct, and one of the kilns when regulated in this way gave splendid results. It was found, however, that in most cases it was better to allow a little more than 100 per cent. opening to allow for stoppages occasioned by an accumulation of sand, brick dust, etc. We will not

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go into all that however, or into the variations it was found necessary to make in this to meet conditions in slightly different kilns. The same principles were adapted to meet the conditions in thirty and thirty-four foot round kilns with equal success.

The portion of the main flue tributary to the small stacks was handled in the same way, the following tables being worked out:

PRELIMINARY CALCULATIONS.

$D = 26.4$

$a = 5''$, etc.—same as portion leading to large stack.

Size of opening	b dimensions	Diameter of equivalent circle or "d"	Number of openings of this size main flue will take	Percentage each one is of the whole
"Two brick out"	5.5	6.0″	39	2.5
"Three brick out"	8.0	7.0″	27	3.7
"Four brick out"	11.0	8.0″	19	5.2
"Five brick out"	14.0	9.0″	14	7.1
"Six brick out"	16.5	9.6″	11	9.0

From this, the following arrangement is worked out:

Openings into Portion of Main Flue Tributary to Small Stacks.

Number of openings one side of flue	Number of openings both sides of flue	Number of "brick out"	Percentage of openings
4	8	3	29.6
4	8	4	41.6
1	2	5	14.2
1	2	6	18.0
Total 10	20		103.4

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FLOOR REGULATION.

When the flues are properly regulated there is not so much necessity of regulating the openings in the floor. The number and size of floor openings is a question much discussed, especially by the so-called "dead bottom" advocates. We assumed that properly regulated flues made the bottom regulation unnecessary. We tried, however, cutting down the number of openings by cross-setting the bottom brick in such a way as to block off about half the floor opening. In some of the kilns about half the floor openings were plugged until the actual floor opening equaled the theoretical. This was found to be very beneficial. The only difficulty is that unless a very complicated system is adopted, no allowance is made for the nearness to, or remoteness from, the stack. The same formulae are used as in the case of the floor regulation, and, for the Long kilns, figures out as follows:

CALCULATIONS.

Square feet of floor taken care of by N flue (leading to one large stack) 983
Number of openings in floor, 1 by 5 inches (before regulation) 2850
Diameter main flue or D..... 42.298″
Diameter floor opening or *d*..... 2.37 ″
Number of *d*'s D will best take care of, or N.... 1352 ″

If we block up half the openings we will have 1425 or a trifle more than the number theoretically correct.

The same method is applied to the portion of the floor tributary to the small stacks, the diameter of one small stack being taken as *d* as follows:

Square feet of floor taken care of by *n* flue (leading to one small stack)..... 201
Number of openings in floor 1, by 5 inches (before regulation) 582.9
Diameter effectual main flue, or D..... 26.43*z*″
Diameter floor opening, or *d*..... 2.37*z*″
Number of *d*'s D will best take care of, or N. 415.5

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If we block up half the openings we will not have enough, so, theoretically, we should block off about every fifth opening.

THE RESULT.

This system of regulation was applied, with more or less modification to suit conditions, to twenty-one kilns having five distinct types of bottoms. An average of the three burns made on each kiln immediately following the regulation showed an increase in first-quality pavers of 8.7 per cent. The reduction in amount of coal used is noticeable, and the burning is held more nearly to schedule. The regulation, we feel, has, on the whole, more than justified itself.

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A STUDY IN UNDERGLAZE COLORS WITH VIEW OF DETERMINING THE MOST INSOLUBLE AND NON-VOLATILE UNDERGLAZE COLOR COMPOSITION.[1]

By EARL T. MONTGOMERY.

OBJECT OF THE INVESTIGATION.

The object of this investigation was to determine the most insoluble and non-volatile underglaze color fritt composition. Of the literature on this subject I believe we only have Roesler's statement, quoted by Seger, that a compound of the spinel composition is the most resistent to the dissolving action of the glaze. The spinel proper is $MgO.Al_2O_3$. Seger advised the compounding of underglaze colors, wherever possible, according to the spinel formula: either a metallic monoxide with the sesquioxide of alumina, or a metallic monoxide with a metallic sesquioxide. The work here was undertaken to verify this.

SCOPE OF THE RESEARCH.

In order to cover the field as systematically as possible, it was decided to compound the oxides, and wherever desirable, the phosphates of the six most commonly used metals, with four inert or refractory elements in five different proportions, one being according to the spinel formula and with two proportions above and two proportions below the spinel. These color fritts were to be calcined at a high heat, ground and washed, then compounded, with 20 per cent., by weight, of the glaze to be used over them, and then fired under glaze and on biscuit under two conditions, the first being the American practice of high biscuit and low glost, and the second being the European practice of low biscuit and high glost.

[1] See article by Edward C. Storer, p. 115, Vol. V, Trans. A. C. S., on investigation quite similar to this.—Editor.

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SCHEME OF COMPOUNDING AND SYSTEM OF MARKING.

Six oxides and three phosphates were used, designated by letter from A to J inclusive. Four refractory elements or substances were used, designated by the Roman numerals I to IV inclusive; and the five proportions between coloring oxide, or phosphate, and the refractory substances, by the Arabic numerals 1 to 5 inclusive, as follows:

		0.50 eqv. refractory substance (1)
	O.	0.75 eqv. refractory substance (2)
1.0 R		1.00 eqv. refractory substance (3)
		1.25 eqv. refractory substance (4)
		1.50 eqv. refractory substance (5)

The following table, No. 1, gives the list of oxides or phosphates used, their designating letter and their chemical formula. Table No. 2 gives the list of refractory substances used and the data for each as in Table No. 1.

Table No. 1. Metallic Oxides and Phosphates.

Letter	Coloring oxide or phosphate	Formula
A	Chromium oxide	Cr_2O_3
B	Chromium phosphate	$Cr_2(PO_4)_2$
C	Cobalt oxide	Co_3O_4
D	Cobalt phosphate	$Co_3(PO_4)_2 + 2(H_2O)$
E	Copper oxide	CuO
F	Ferric oxide	Fe_2O_3
G	Ferric phosphate	$Fe_2(PO_4)_2 + 8(H_2O)$
H	Manganese oxide	MnO_2
J	Uranium oxide (yellow)	$Na_2U_2O_7 + 6(H_2O)$

Table No. 2. Inert or Refractory Substances.

Number	Substance	Formula
I	Aluminium oxide	Al_2O_3
II	Silica	SiO_2
III	Aluminium phosphate	$Al_2(PO_4)_2$
IV	Kaolin	$Al_2O_3.2SiO_2.2H_2O$

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In order to make this plan of compounding more comprehensive, the following table of actual weights is given for chromium oxide, as an example.

	1	2	3	4	5
I	152 Cr_2O_3	152 Cr_2O_3	152 Cr_2O_3	152 Cr_2O_3	152 Cr_2O_3
	51 Al_2O_3	76.5 Al_2O_3	102 Al_2O_3	127.5 Al_2O_3	153 Al_2O_3
II	152 Cr_2O_3	152 Cr_2O_3	152 Cr_2O_3	152 Cr_2O_3	152 Cr_2O_3
	30 SiO_2	45 SiO_2	60 SiO_2	75 SiO_2	90 SiO_2
III	152 Cr_2O_3	152 Cr_2O_3	152 Cr_2O_3	152 Cr_2O_3	152 Cr_2O_3
	122 $Al_2(PO_4)_2$	183 $Al_2(PO_4)_2$	244 $Al_2(PO_4)_2$	305 $Al_2(PO_4)_2$	366 $Al_2(PO_4)_2$
IV	152 Cr_2O_3	152 Cr_2O_3	152 Cr_2O_3	152 Cr_2O_3	152 Cr_2O_3
	129 Kaolin	193.5 Kaolin	258 Kaolin	322.5 Kaolin	387 Kaolin

As a final distinguishing mark, the letters F and R are added, to designate the type of glaze used over the given trial and incidentally the biscuit and glost heat treatment of that trial. An example would be thus: A—I—1—F and A—I—1—R. F stands for fritted glaze and, therefore, for the American practice of high biscuit and low glost. R stands for raw porcelain glaze and, therefore, for the European practice of low biscuit and high glost. As each trial piece was dipped only half over with glaze, the effect on biscuit and underglaze is, of course, given on the same trial and no mark is needed to designate the two conditions.

The Body and Glazes Used.

The body used for the trial pieces was a good low feldspar porcelain, of the following composition:

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Eng. ball clay	15.0%
Eng. china clay	25.0
Flint	43.5
Feldspar	15.0
Magnesium carbonate	1.5
	100.0

It was quite translucent.

The trials were jiggered discs of about 3.5 inches fired diameter. This shape was decided on so that the colors could be put on in concentric rings, on a whirler, by means of a soft brush. Half of the trials were biscuited at cone 10 for the hard biscuit, and half at cone 05 for the soft biscuit.

The fritted glaze used for the high biscuit and low glost trials was the glaze given by Mr. Earnest Mayer in Vol. I, *Trans. A. C. S.*, as follows:

$$\left.\begin{matrix} 0.0640\ K_2O \\ 0.1920\ Na_2O \\ 0.4903\ CaO \\ 0.2534\ PbO \end{matrix}\right\} 0.2811\ Al_2O_3 \left\{ \right. \left.\begin{matrix} \\ \\ 0.3845\ B_2O_3 \end{matrix}\right\} 2.8070\ SiO_2$$

The trials over which this glaze was used were fired in the glost burn to cone 02, this being the heat at which the glaze matured in the test kiln.

The raw porcelain glaze used for the low biscuit and high glost trials was the following typical porcelain glaze:

$$\left.\begin{matrix} 0.3\ K_2O \\ 0.7\ CaO \end{matrix}\right\} 0.4\ Al_2O_3\ \{3.825\ SiO_2$$

The trials over which this glaze was used were fired in the glost burn to cone 12.

Preparation of the Colors.

The color fritts were thoroughly wet-ground in an agate mortar. They were then dried and calcined at cone 10 in covered, biscuit-porcelain crucibles. The calcined color fritts were finely ground, thoroughly washed with water, dried, compounded with 20 per cent., by weight,

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of the glaze, and again intimately wet-ground. The colors were then ready for use.

Using 9 coloring oxides or phosphates, and each being compounded in 20 different proportions with a refractory substance, give 180 color fritts which were prepared and calcined. All of the color fritts, which stood the calcining heat of cone 10 without fusing or becoming too hard for use as colors, were prepared as given above and applied as follows:

The five combinations of each color with each one of the refractory substances were applied in five concentric circles on a hard biscuit disc for the low glost burn and also on a soft biscuit disc for the high glost burn. One trial would then be marked thus: A—I—1 to 5—F, and the other: A—I—1 to 5—R, the numerals 1, 2, 3, 4 and 5, reading on the trial from the outside circle of color to the central one.

SUMMARY OF RESULTS.

Statement of Condition of Color Fritts after Calcining at Cone 10.

Mark	Condition of fritt	Color
A I—1 to 5	Fine soft powder.	Bright light green.
A II—1 to 5	Soft powder. Little harder than A-I.	Bright light green.
A III—1 to 5	Soft sintered powder. Harder from 1 toward 5.	Rich dark green.
A IV—1 to 5	Hard cake. Scratches with difficulty with knife.	Light green.
B I—1 to 5	Fairly hard cake.	Dark buish green.
B II—1 to 5	Sintered powder. Much softer than B-I. Softer 1 toward 5.	Bright dark green.
B III—1 to 5	Hard vitreous globules.	Dark green.
B IV—1 to 5	Hard vitreous crackled cake.	Light grass-green.
C I—1 to 5	Soft sintered cake. Softer 1 to 5.	Fine navy-blue.
C II—1 to 5	Hard sintered cake.	Salmon-pink.
C III—1 to 5	Hard vitreous fusion.	Rich purple.
C IV—1 to 5	Hard vitreous crackled cake.	Bluish gun-metal color.

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Statement of Condition of Color Fritts after Calcining at Cone 10 (*Continued*).

Mark	Condition of fritt	Color
D I—1 to 5	Hard vitreous bubbled fusion to hard crackled cake.	Deep purple.
D II—1 to 5	Hard crackled cake to hard sintered cake. Softer than D-1.	Old rose.
D III—1 to 5	Hard vitreous globules.	Purple.
D IV—1 to 5	Hard vitreous fusion.	Gun metal.
E I—1 to 5	Hard sintered crackled cake.	Metallic gray.
E II—1 to 5	Hard vitreous fusion to hard sintered cake.	Greenish gray.
E III—1 to 5	Hard vitreous fusion.	Metallic gray (crystallized).
E IV—1 to 5	Hard vitreous crackled cake.	Greenish gray.
F I—1 to 5	Hard vitreous cake to soft sintered cake.	Reddish brown.
F II—1 to 5	Hard vitreous fusion to hard crackled cake.	Purplish brown.
F III—1 to 5	Hard vitreous fusion.	Metallic gray (crystallized).
F IV—1 to 5	Hard vitreous globules.	Greenish black.
G I—1 to 5	Hard vitreous cake to fairly hard crackled cake.	Reddish brown.
G II—1 to 5	Hard vitreous fusion.	Reddish brown.
G III—1 to 5	Hard vitreous fusion.	Greenish brown.
G IV—1 to 5	Hard vitreous fusion.	Brown.
H I—1 to 5	Hard crackled cake to sintered cake.	Brown.
H II—1 to 5	Hard vitreous fusion.	Brownish gray.
H III—1 to 5	Hard vitreous fusion to bubbled fusion.	Light brown.
H IV—1 to 5	Hard vitreous fusion to hard crackled cake.	Dirty dark brown.
J I—1 to 5	Hard sintered cake. Softer 1 to 5.	Yellowish gray.
J II—1 to 5	Hard vitreous globules.	Yellowish gray.
J III—1 to 5	Hard vitreous globules.	Yellowish green.
J IV—1 to 5	Hard crackled cake.	Yellowish black.

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RESULTS OF THE GLOST BURNS.

Series A.—None of these colors flowed under the glaze at either heat. No volatilization was noticeable. Fine green colors.

Series B.—None of these colors, which gave workable color fritts, flowed under the glaze at either heat. No volatilization was noticeable. Fine green colors.

Series C.—C–I and C–II, which gave workable color fritts, showed some tendency to flow at both heats. No volatilization was noticeable. Fine dark blue colors.

Series D.—D–I and D–II, which gave workable color fritts, did not flow at either heat. No volatilization was noticeable. Fine dark blue colors.

Series E.—E–I and E–II, which gave workable color fritts, gave a flowed green at the low heat and a black color widely disseminated through the glaze at the high heat. Volatilization was noticeable.

Series F.—F–I and F–II, which gave workable color fritts, did not flow at either heat. Volatilization not noticeable. Good yellow at low heat and a dark brown color at the high heat.

Series G.—G–I, which was a workable color fritt, did not flow at either heat. Volatilization not noticeable. Good brown color.

Series H.—H–I, which was a workable color fritt, did not blow at either heat. Volatilization noticeable at high heat but not at low. Typical manganese-brown at both heats but very light at high heat, due to volatilization.

Series J.—J–I, which was a workable color fritt, did not flow at either heat. No volatilization noticeable but color was not good. Grayish yellow-brown.

DISCUSSION OF DATA AND RESULTS.

In regard to the relative merits of the four refractory substances used to produce insoluble and non-volatile color fritts, we see that, in most all cases, Al_2O_3 is the best

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refractory. An exception is noted in case of the phosphates of the metals, in which cases, SiO_2 gives the most refractory color fritt and the most insoluble color. Where the color itself is refractory, as in the case of Cr_2O_3, any of the refractories can be used. In many cases, good workable color fritts were obtained with both Al_2O_3 and SiO_2. The most refractory color fritts gave, in all cases, the most insoluble colors.

No distinction could be made, in the appearance of the color, between the mixtures made in the five different proportions of the refractory substance and colorant. The workable color fritts appeared to be equally insoluble and equal in shade of color for all of the proportions used. This being true, it is possible in some cases to get a more refractory color fritt by going above the spinel ratio in compounding the fritt.

Volatilization of a color seems to be a function of the given coloring oxide or phosphate and is not much affected by compounding and calcining with a refractory substance. Of course, in this study, this statement could not be proven quantitatively and is only given as a suggestion.

As a general rule, the oxides of the metals seem to give the most insoluble and best working colors. An exception was noted in the case of cobalt where the phosphate gave the most insoluble color.

Color fritts calcined at cone ten seem to stand either heat treatment equally well in the glost burn, without being affected in regard to solubility.

In closing, the writer desires to express his deep appreciation of the many helpful suggestions given during the progress of the work by Prof. A. V. Bleininger, Director of the Department of Ceramic Engineering, University of Illinois, and of the granting of the necessary funds of the department.

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THE EFFECT OF FELDSPAR ON KAOLIN IN BURNING.[1]

By JOSEPH KEELE, Ottawa, Ont.

The following experiments were undertaken to show the effect of addition of feldspar to a china clay, when burned at different temperatures within the range used in pottery bodies.

The feldspar was added in varying amounts and also in different sizes of grains.

The materials used were the washed kaolin, known as English china clay, and microcline feldspar from the Villeneuve mine, Province of Quebec. The chemical composition of each of these is given below.

Analysis of the Materials Used.

Kaolin		Feldspar	
SiO_2	46.46	SiO_2	62.76
Al_2O_3	38.86	Al_2O_3	20.40
Fe_2O_3	0.58	FeO	0.05
	....	MnO	trace
MgO	trace	MgO	0.36
CaO	0.00	CaO	0.40
K_2O	1.37	K_2O	13.38
Na_2O	0.63	Na_2O	2.69
H_2O	13.41	H_2O	0.40
	101.31		100.44

Test pieces of the feldspar, ground to pass a 100-mesh sieve, and burned to cone 7, had a glassy appearance, with granular structure, but were not deformed. When burned to cone 9, the test pieces were melted to a glass.

The feldspar was prepared by grinding it in a jaw crusher, and then sifting the ground material through a set of sieves.

Six different sizes of grains were used as follows:

[1] See E. Berdel, Sprechsaal, No's 5, 6, 18-24, 1904; Dr. Simonies, Sprechsaal, No. 29, 1907 (Ed.).

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1. 40 mesh: through 40-mesh sieve, held on 60 mesh
2. 60 mesh: through 60-mesh sieve, held on 80 mesh
3. 80 mesh: through 80-mesh sieve, held on 100 mesh
4. 100 mesh: through 100-mesh sieve, held on 150 mesh
5. 150 mesh: through 150-mesh sieve, held on 200 mesh
6. 200 mesh: through 200-mesh sieve, held on ... mesh

The sifting was repeated to secure as perfect a separation as possible of the various sized grains.

Mixtures of the kaolin with 10, 20, 30 and 40 per cent. respectively of each size feldspar grains were prepared. These were then mixed with distilled water to the proper consistency and moulded into bricklets 4″ x 1″ x 3/6″.

After drying and weighing the green test pieces, they were saturated in kerosene, and their volume determined in a Seger volumeter.

All the bricklets were burned to cone 010 in 12 hours in an oil kiln.

The subsequent burnings were all done in a Seger gas-fired "rund-ofen," the time varying from three hours for cone 05 to eight hours for cone 12.

The same bricklets were carried through from the green state to each successive temperature.

Measurements of volume, dry and saturated weight were made after each burning, from which the porosity and volumetric shrinkage were calculated by the following formula:

$$\text{Per cent. porosity} = \frac{W' - W}{V},$$

in which W = dry weight,
W' = saturated weight,
V = volume.

$$\text{Per cent. volumetric shrinkage} = \frac{V - V'}{V},$$

where V = volume of dry green brick,
V' = volume after burn in question.

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Table I. Kaolin-Feldspar Mixtures—Porosity Table.

Size of mesh feldspar	Percentage of feldspar	Green	0.5	1	3	5	7	9	12
40	40	31.00	34.50	31.70	27.55	23.65	19.60	10.95	4.96
	30	33.63	37.30	30.95	28.55	25.40	21.70	14.40	9.33
	20	36.60	40.00	37.15	32.00	30.00	25.40	18.45	14.21
	10	39.50	43.00	40.00	35.70	32.35	30.50	23.00	18.65
60	40	33.08	35.50	32.00	27.35	24.10	19.05	9.70	4.65
	30	34.00	37.31	30.40	28.80	25.85	21.15	15.10	8.93
	20	37.75	39.50	38.40	34.60	29.50	24.25	19.25	11.75
	10	39.20	41.55	39.50	35.10	32.50	27.75	24.00	17.55
80	40	32.70	35.50	31.00	25.30	22.65	15.75	10.45	6.36
	30	35.00	36.80	32.90	27.80	23.30	19.35	14.45	9.46
	20	38.45	39.75	36.95	34.10	30.00	26.70	17.60	10.50
	10	38.75	41.70	40.00	29.40	28.10	27.60	20.30	14.31
100	40	32.85	36.50	30.80	23.80	17.10	13.20	6.60	1.40
	30	35.20	39.00	38.30	29.40	25.05	18.30	10.80	4.92
	20	37.00	41.00	38.40	30.60	27.50	22.10	14.40	8.87
	10	39.20	42.70	38.15	34.55	32.25	25.30	22.95	16.37
150	40	33.40	36.85	21.60	19.10	16.50	9.30	5.80	0.00
	30	35.00	38.80	31.70	26.30	23.00	15.10	11.50	6.00
	20	37.20	39.00	35.00	29.10	25.30	22.50	14.50	9.00
	10	39.30	43.30	38.15	32.25	30.35	25.10	21.00	15.66
200	40	35.10	38.60	22.65	18.50	14.80	6.00	0.00	0.00
	30	36.45	40.00	28.80	20.50	15.80	13.65	4.40	0.00
	20	38.05	41.55	33.60	28.45	23.70	21.90	10.50	7.11
	10	41.10	43.80	36.70	33.15	28.25	27.08	17.20	12.75
Kaolin		41.00	44.20	43.50	39.00	35.93	33.30	29.44	24.42

When the feldspar-kaolin mixtures were first heated they became more porous until the temperature of cone 05 was reached. The increased porosity of the bodies at this temperature is probably due to dehydration or expulsion of water from hydrous clay minerals. When the period of dehydration is complete, all of the mixtures, as well as the pure kaolin body, become denser in burning until at cone 1 they are as dense, or more so, than they were in the green state. From cones 1 to 12 they show a regular increase in density as each successively higher temperature is reached.

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The results of the porosity tests are given in Table I, and are also shown graphically in the diagram, Figs. 1 to 6. Though there are some irregularities, due to experimental errors, the porosity curves of each group are fairly consistent with one another.

It becomes evident, as burning progressed, that cavities were forming in the body of the bricklets which were not accessible to water, so that the results given are not the true, but the apparent porosities.

Table II. Kaolin-Feldspar Mixtures, Per cent. Volumetric Shrinkage

Size of mesh feldspar	Percentage of feldspar	Cones						
		0.5	1	3	5	7	9	12
40	40	2.35	6.75	10.70	13.40	17.55	18.65	25.94
	30	3.55	11.80	14.35	16.55	21.00	25.00	30.00
	20	4.15	9.80	15.15	16.15	22.20	27.80	31.55
	10	5.35	12.05	16.45	19.15	22.60	30.00	33.21
60	40	2.10	8.00	11.90	15.50	20.40	29.35	32.20
	30	3.15	12.35	13.20	16.65	21.65	27.75	32.73
	20	5.95	8.70	12.45	19.50	25.55	30.35	35.73
	10	7.80	10.00	15.30	20.00	26.20	30.00	34.45
80	40	3.00	9.50	14.50	17.70	24.05	28.85	30.95
	30	2.75	9.25	13.65	19.40	23.25	28.50	30.00
	20	6.50	12.00	14.65	21.00	25.40	32.25	37.00
	10	8.30	10.00	22.70	24.45	27.95	31.30	36.38
100	40	1.30	9.05	14.90	21.95	25.00	30.00	33.57
	30	1.25	3.45	13.75	18.50	24.40	30.12	35.00
	20	3.05	7.70	16.95	20.10	25.00	31.20	36.86
	10	5.50	12.95	17.75	21.50	29.55	31.60	36.14
150	40	1.25	19.65	20.35	25.00	30.90	33.20	34.48
	30	1.75	11.85	17.20	20.90	30.00	32.45	34.95
	20	....	.....	.....	.....	.....	.....	.....
	10	4.90	11.75	20.25	22.65	28.50	32.70	35.75
200	40	1.30	20.50	24.40	28.20	35.25	37.00	39.04
	30	2.30	16.18	26.15	29.90	32.30	37.70	39.40
	20	3.70	13.45	21.45	25.75	28.10	36.00	39.25
	10	5.60	14.60	21.05	24.75	28.80	37.25	39.63
Kaolin		10.00	11.75	17.00	21.30	24.75	27.46	31.34

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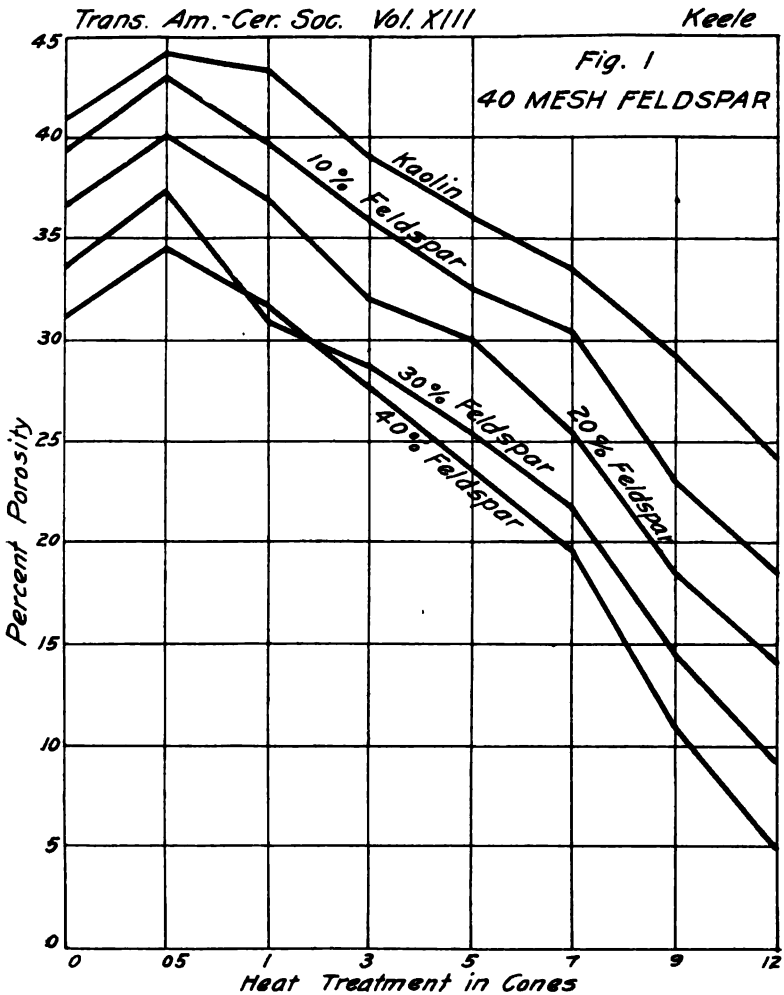

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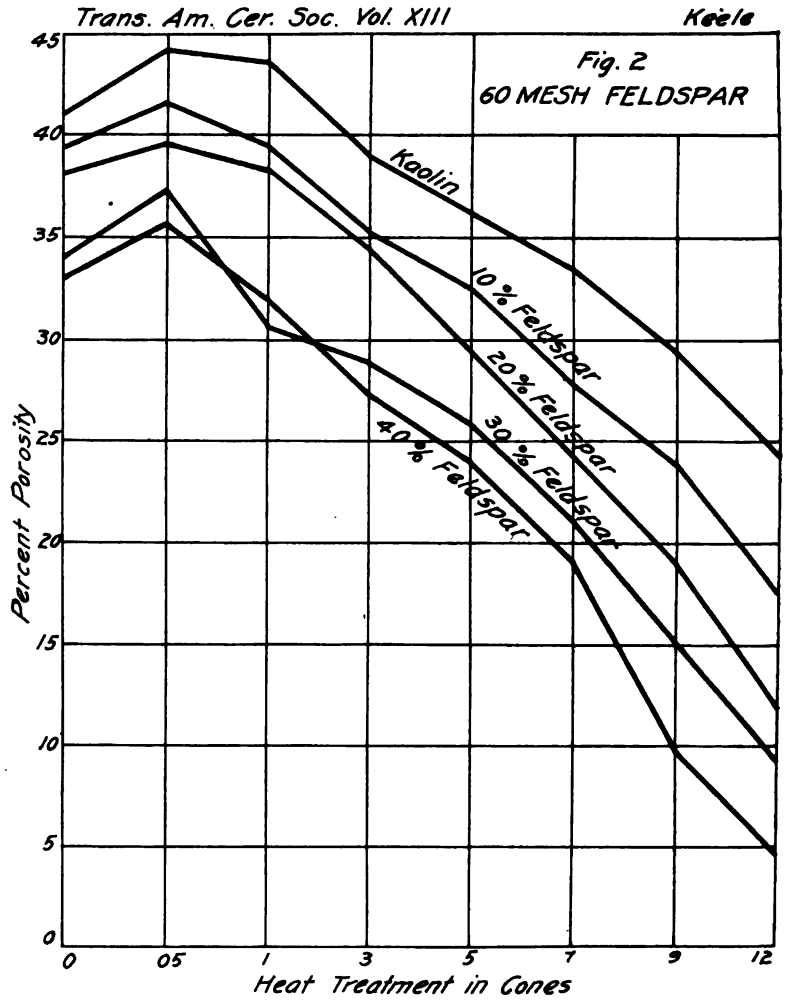

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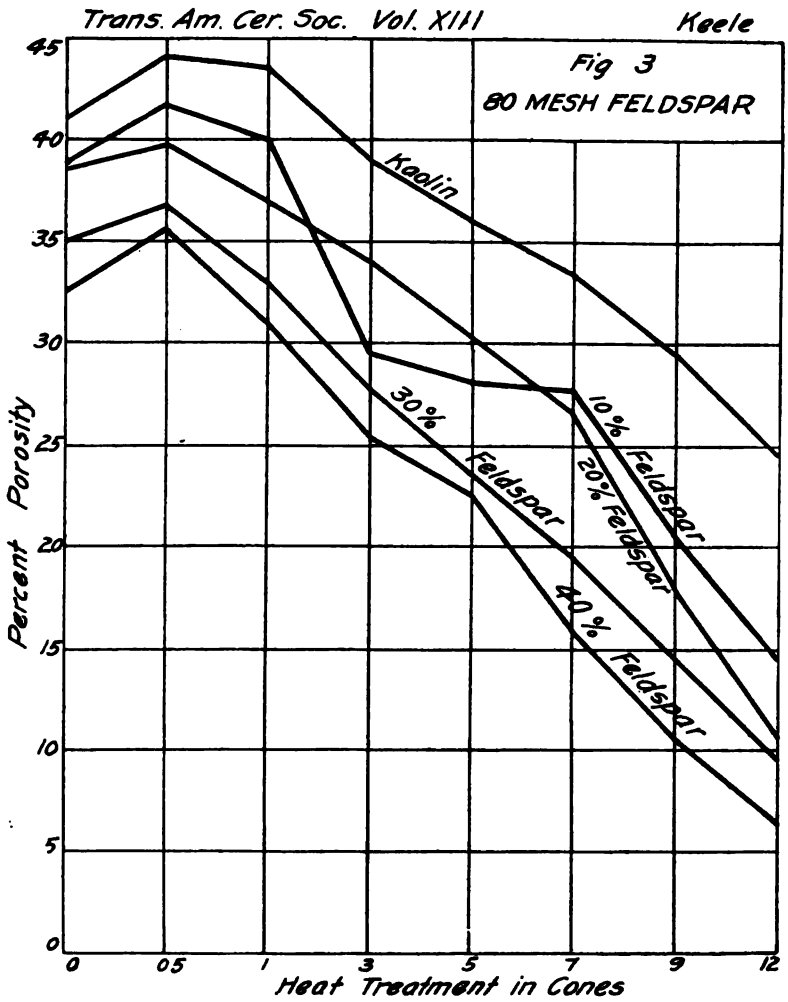

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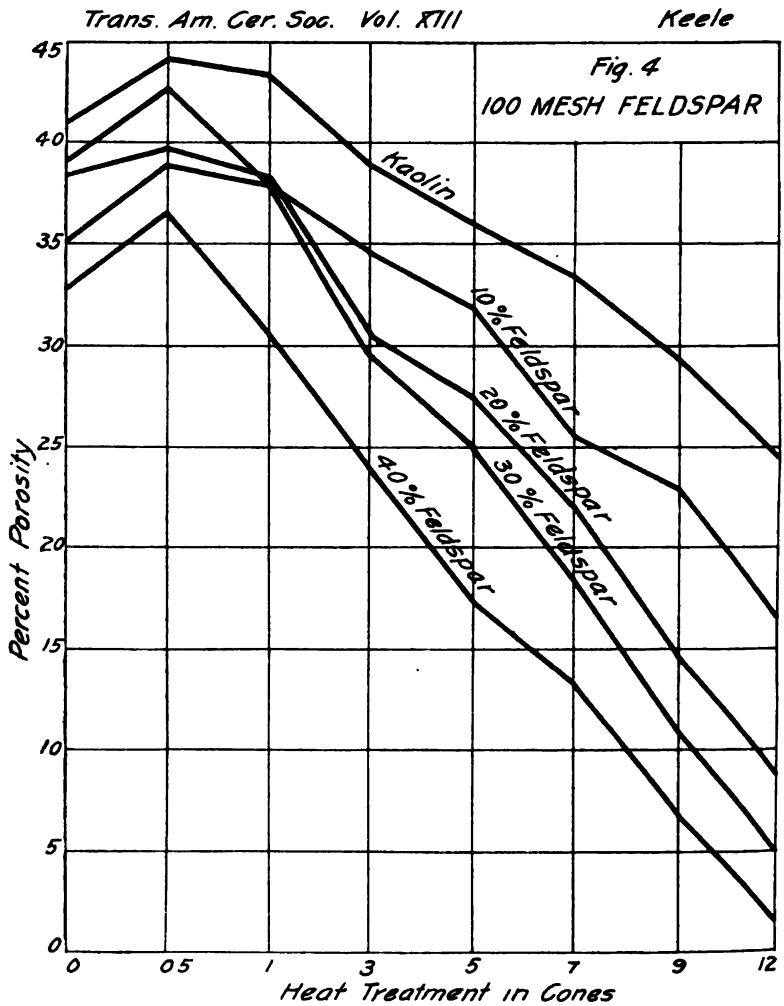

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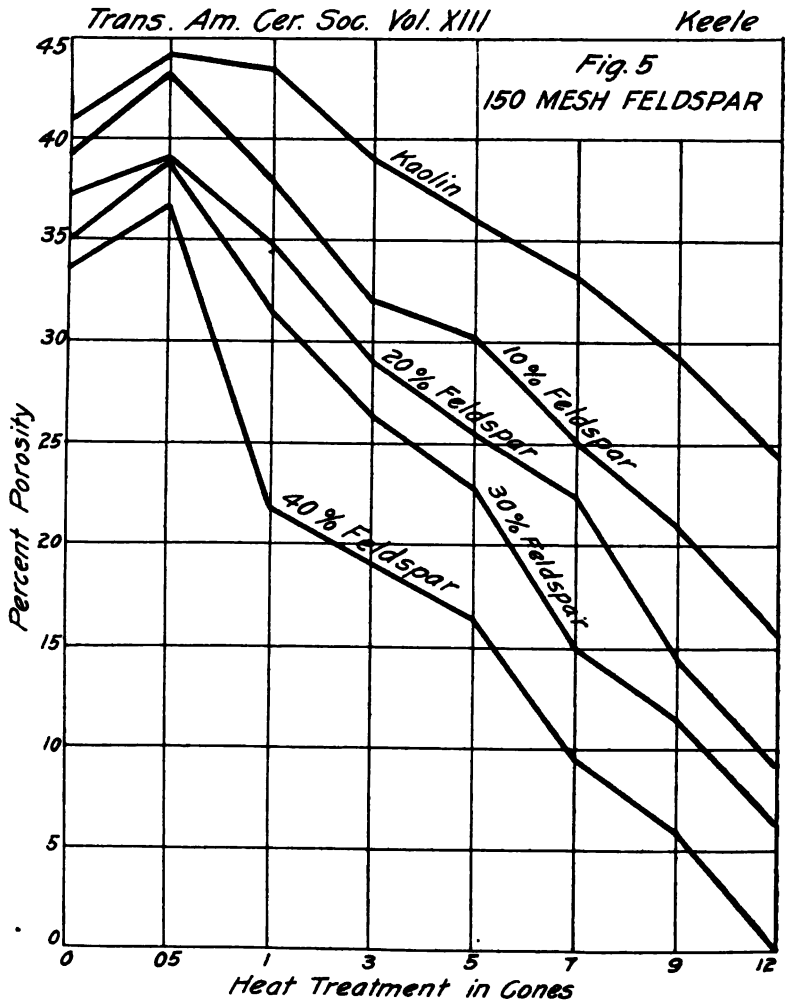

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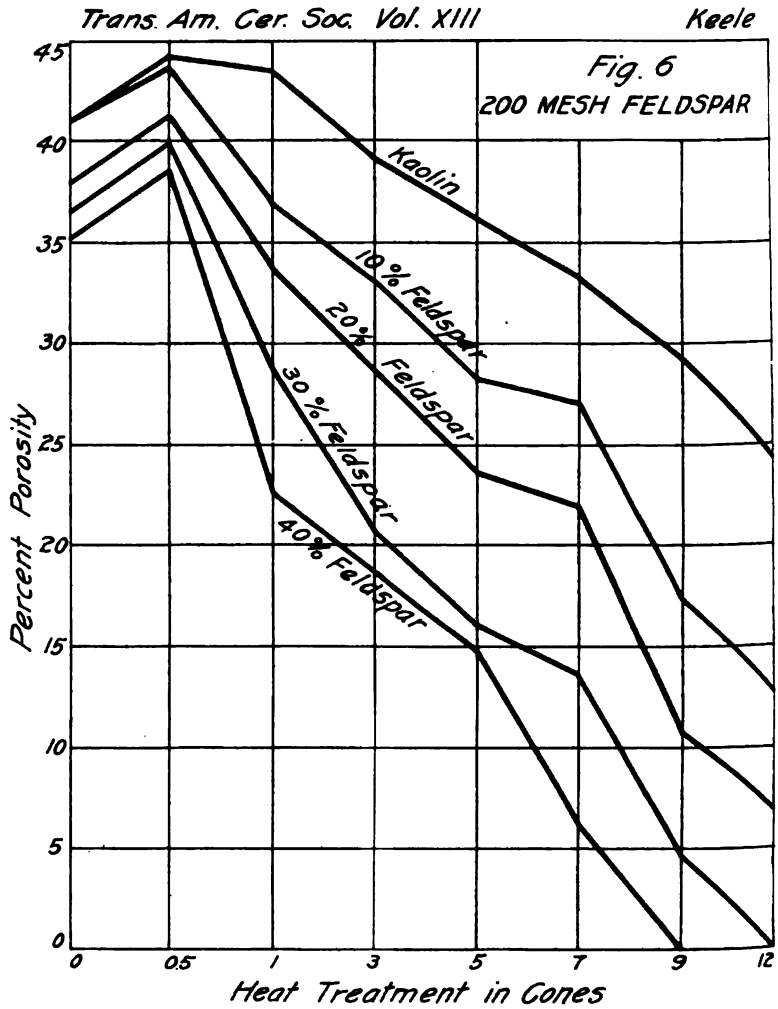

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In general, the porosity increases rather uniformly with decrease of feldspar. There is also a decrease in porosity with the use of finer grained feldspar.

Owing to the difficulty of obtaining uniform sized grains of feldspar for the different mixtures, the effect of size of grain on porosity is not very pronounced until two mixtures containing rather widely separated sizes of feldspar grains are compared.

Feldspar which was coarser in grain than 150-mesh, did not give a vitrified body in any of the mixtures at any temperature reached in the experiments. As was expected, vitrification seems to proceed more rapidly and approach completion earlier in the mixtures which contained the finest grained feldspar.

The results for volumetric shrinkage, Table II, are rather erratic, the coarser grained mixtures showing the most irregularity. The development of gas bubbles in the body might account for swelling at points where contraction was ordinarily expected to occur.

In the mixtures containing the coarser grained feldspar, the shrinkage becomes greater as the amount of feldspar used becomes less, the feldspar in this case acting somewhat like sand in an ordinary clay body. In the two mixtures containing the finest feldspar, the tendency toward higher shrinkage seems to accompany an increase in feldspar, being the reverse of the action of the coarse grains.

That a decided fluxing action begins at low temperatures is shown by the decrease in porosity of all the mixtures between cones 05 and 1, the decrease being particularly pronounced in 150- and 200-mesh feldspar mixtures (Figs. 5 and 6).

Recent experiments have shown that the potash-rich feldspar do not have a definite melting point as metals do.

Fusion tests made on finely powdered microcline in the geological laboratory of the Carnegie Institution[1]

[1] Day, A. L., and Allen, H. T., "The Isomorphism and Thermal Properties of the Feldspars," Publ. No. 31, Carnegie Inst. of Washington, 1905, pp. 13 to 15, also Am. Jour. Sci., 4th Ser., Vol. 19, pp. 93–144, 1905.

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showed that at 1,000° C. traces of sintering were evident; at 1,075° the powder had formed a solid cake; at 1150° this cake had softened somewhat; and at 1,300° C. it had become a viscous liquid which could be drawn out into glassy threads. In most of the determinations, complete fusion of feldspar has taken place in a dry state at temperatures below Seger cone No. 9 which fuses at about 1310° C. or 2390° F.

Concerning the behavior of clays below 1000° C., J. M. Knote[1] suggests that "on dehydration, kaolinite or clay substance breaks down into two silicates, one rich in alumina, and the other rich in silica. These silicates are readily attacked by reagents. At about 950° C. a pronounced change takes place, the exact nature of which is still uncertain. If $Al_2O_3.2SiO_2$ is formed at this temperature, it becomes unstable as the temperature advances and is decomposed by the action of fluxes, with the formation of a basic and an acid silicate. If no combination of silicates takes place at 950° C. and the change is due to the formation of isomeric compounds, it is not so easy to explain the phenomena so often pointed out."

Two materials may begin to react and gradually flux together at temperatures below the melting point of either. Messrs. Heath and Mellor[2] have shown that finely ground feldspar, softening at 1150° C., begins to react with finely ground quartz and china clay below 1000° as indicated by the presence of glassy patches in mixtures which have been heated to this temperature.

As the higher temperatures are reached in burning, the nature of the fluxing action appears to be an elaboration of the initial stages: As soon as there are evidences of fusion of the feldspar grains, they become surrounded with rims of molten solution of china clay. There is also a tendency for the molten feldspar rims to increase

[1] Knote, J. M., "Some Chemical and Physical Changes in Clays Due to the Influence of Heat." Am. Cer. Soc., Vol. XII.

[2] Arthur Heath and J. W. Mellor, "The Action of Heat on Binary Mixtures of Feldspar Flint, and China Clay," Trans. Eng. Cer. Soc., Vol. VII, pp. 80–100.

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the surface tension of the clay particles in their neighborhood, drawing particles together, thus causing a decreased porosity and increased shrinkage.

Under the influence of severe heating, all clay wares develop a somewhat crystalline structure. In the feldspar china clay reactions, crystals of minerals resembling sillimanite (Al_2SiO_5) are formed. Beyond this nothing has been observed, as either the point to which pottery bodies are carried in practice or the rapid rate of cooling do not admit of other crystals being formed.

Quoting from the writers last referred to, regarding their examination of microscopic sections made from china clay feldspar bodies after burning to different temperatures: "This enabled us to watch the zone of vitrification at the surfaces of contact between the bright fragments of crystalline feldspar and the china clay. It is interesting to observe the gradual progress of the reaction between the feldspar and china clay. This is brought out by the changes in the outlines of the fragments of feldspar which are in focus. At the higher temperatures, the surfaces of the feldspar in contact with the china clay were much eroded; part of the feldspar seems to be 'sucked up' by the clay and part seems to form a glassy mass with clay. At 1200° the feldspar had nearly disappeared and crystals of sillimanite began to appear."

The action then that goes on in the heated body appears to be the gradual absorption of kaolin by the molten feldspar. The fine grinding evidently facilitates and accelerates the absorbing capacity of the feldspar, as it exposes a greater surface for reaction with the clay particles.

The coarse grains of feldspar are isolated in the clay matrix and only come into contact with and absorb a limited number of clay particles, so that quite a portion of the clay in the bodies did not become affected by the feldspar at all, which explains the lack of vitrification in bodies containing 40- to 100-mesh feldspar.

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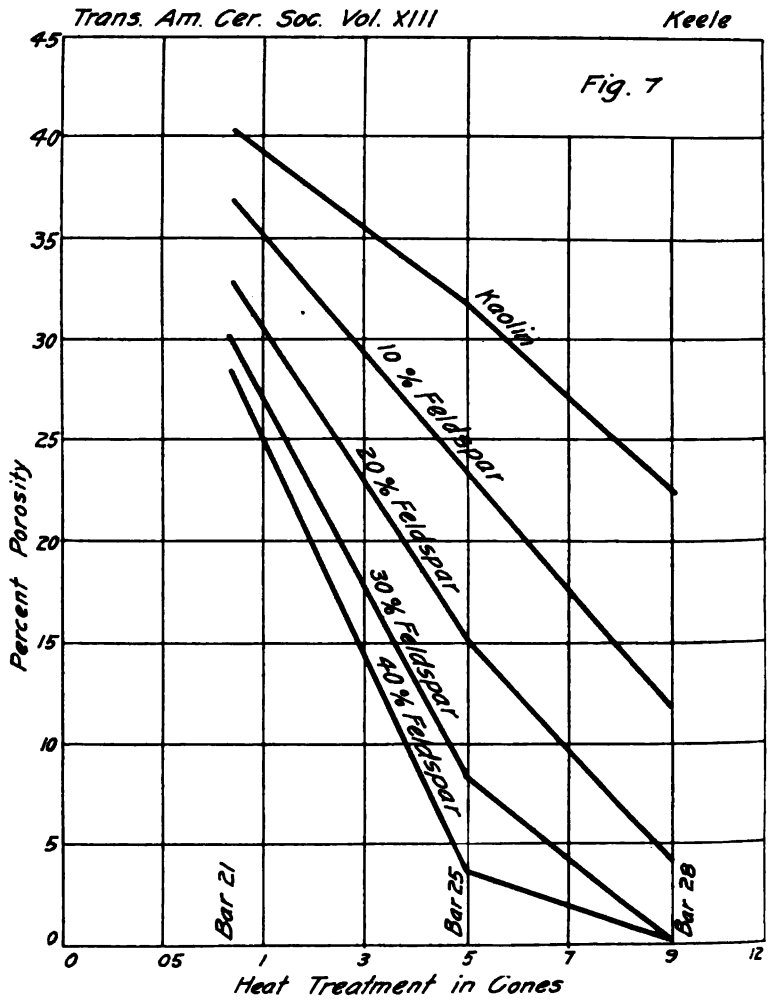

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Referring to the diagrams (Figs. 1 and 6) it is seen that 20 per cent. of 200-mesh feldspar causes the same amount of vitrification as 40 per cent. of 40-mesh.

In pottery bodies, the feldspar is the constituent relied on to cement the ingredients together at high temperatures. If present in coarse grains it will have to flow to fill the various pores, and reach the grains of quartz and clay that it is to cement together, but if finely ground, it will merely have to soften in position.

It follows, then, that the finely ground feldspar requires less time to mature a pottery body, that such a body does not approach so near to fusion, and that the tendency to bending and warping is much reduced.

Time appears to have an effect on the amount of vitrification that feldspar will produce in a clay body at various temperatures. It was found that in burning some of the specimens for a more prolonged period at cone 9, the porosity was reduced from 1 to 3 per cent. It seems very probable that if a sufficient length of time were allowed at the temperature of cone 5, that a degree of vitrification would be arrived at equivalent to that at cone 9 in these experiments. To illustrate the effect of time on vitrification, the curves in Fig. 7 were plotted from tables of figures for porosity published in Messrs. Heath and Mellor's paper, using the same scale as Figs. 1 to 6.

The materials used are almost identical in both cases, but it will be seen that their porosities for corresponding mixtures and temperatures are lower. These experiments were conducted in pottery ovens, and the greater time occupied by the test pieces in these ovens above those burned for short periods in gas kilns would account for this difference.

These experiments were planned under the direction of Professor H. Ries and carried out in the Geological Laboratory of Cornell University at Ithaca.

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SOME PRACTICAL OBSERVATIONS IN THE DRYING OF TERRA COTTA.

By Wm. J. Stephani.

The following observations were made in the factory. For these records we took two pieces of ashlar and three pieces of dental moulding. All the pieces were made by the same man and from the same mix of clay. When turned from the mould they were all true in shape. They were dried on a slat floor drier, commonly known as a pan drier.

The only difference in the drying treatment given these pieces was in the rate at which the shrinkage water was expelled. This was done to determine the effect on the warping of these large pieces, of rushing the early stages of the drying.

The data given in the following tables are not those of shrinkage. They are in terms of 1/100 of an inch, and represent the amount which the pieces were out of alignment at the points indicated on the diagrams in Fig. 1 and Plate No. 1. Measurements were made at different periods of the drying and then, finally, the lowest point of each piece, when dry, was taken as zero and all measurements figured from this point.

THE ASHLAR PIECES.

Seven points were taken on each of the two pieces: four corners, centers of two sides, and center of pieces as shown in Fig. 1.

Lowest point of the piece, when dry, was called zero and all measurements were figured from this point.

In both cases, greatest difference existed between different points at the end of twenty-four hours' drying on account of edges and corners of pieces drying first. Twelve hours later this difference had been greatly reduced and the pieces, when dry, were nearly uniform.

Both pieces, after 24 hours' drying, had taken 65 per cent. of their total drying shrinkage, especially No. 1, which only varied in center of the piece by 3/100 inch

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from the corners and edges. In No. 2, somewhat different results were obtained, the corners (Nos. 1 and 3) going farthest in drying, while 5 and 7 apparently were held up by the center and point No. 6.

Result of piece No. 1: Normal and not unusual in general practice, while in No. 2 we have greater variation due, probably, to the more rapid drying for the first 24 hours, which is shown by the difference in all measurements on the two samples at the end of this period. It is clearly evident from the test that the strain caused in No.

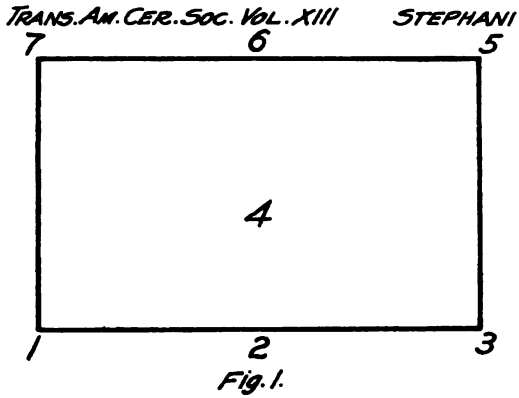

Fig. 1.

2 by rapid drying was too great to overcome, and the piece was never able to get back into the true form.

The data obtained on these two pieces of ashlar are given in the following tables:

Sample No. 1.

Ashlar 2′ 0″ × 1′ 3″ × 4″ thick.

Topographical survey of the surface, giving the rise of various points in the surface, from an assumed datum plane (zero). Heights given in hundredths of an inch.

Point number	1	2	3	4	5	6	7
At end of 24 hours' drying.....	5	6	4	6	9	12	6
At end of 36 hours' drying.....	3	3	3	3	5	4	6
At end of 48 hours' drying.....	3	3	3	0	3	3	3

Observations ended at 48 hours—piece white dry.

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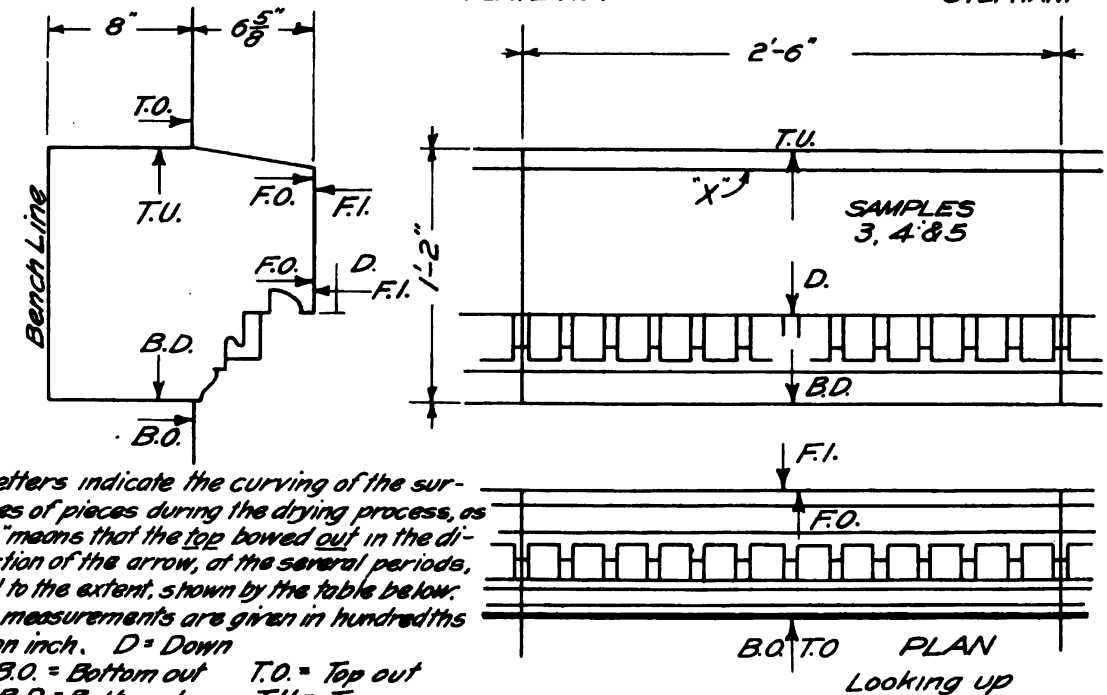
TRANS. AM. CER. SOC. VOL. XIII — PLATE No. 1 — STEPHANI



Letters indicate the curving of the surfaces of pieces during the drying process, as "T.O." means that the top bowed out in the direction of the arrow, at the several periods, and to the extent, shown by the table below. The measurements are given in hundredths of an inch. D = Down

B.O. = Bottom out — T.O. = Top out
B.D. = Bottom down — T.U. = Top up
F.O. = Face out — F.I. = Face in

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Sample No. 2.

Ashlar 2′ 0″ × 1′ 3″ × 4″ thick.

Topographical survey of surface.

Point number	1	2	3	4	5	6	7
At end of 24 hours' drying.....	6	6	3	19	8	20	12
At end of 36 hours' drying.....	2	3	0	14	6	18	8
At end of 48 hours' drying.....	0	3	0	10	6	15	6

Observations ended at 48 hours-piece white dry.

Conclusions.—In this method, two days are required for drying this piece. Therefore, nothing is gained by rushing in the early stages, that is, when the clay is getting rid of its pore shrinkage. By rushing at this time a strain is created, due to uneven drying, from which the piece never recovers.

THE DENTAL MOULDINGS.

The shape and size of the dental mouldings are shown in Plate No. I.

The data obtained in each case are shown in the following tables:

Sample No. 3.

At end of						
24 hours' drying..	B.O. 14	T.O. 12	F.O. 12	B.D. 19	D. 4	T.U. 14
36 hours' drying..	B.O. 14	T.O. 10	F.O. 6	B.D. 12	D. 3	T.U. 12
48 hours' drying..	B.O. 12	T.O. 8	F.O. 0	B.D. 8	D. 3	T.U. 8
60 hours' drying..	B.O. 10	T.O. 6	F.I. 3	B.D. 6	D. 0	T.U. 8
72 hours' drying..	B.O. 6	T.O. 6	F.I. 3	B.D. 6	Up 2	T.U. 6

Observations ended at 72 hours — piece white dry.

Sample No. 4.

At end of						
24 hours' drying..	B.O. 12	T.O. 12	F.O. 6	B.D. 25	D. 6	T.U. 20
36 hours' drying..	B.O. 10	T.O. 10	F.O. 6	B.D. 19	D. 5	T.U. 15
48 hours' drying..	B.O. 10	T.O. 8	F.O. 3	B.D. 12	D. 3	T.U. 12
60 hours' drying..	B.O. 6	T.O. 8	F.O. 0	B.D. 6	D. 0	T.U. 8
72 hours' drying..	B.O. 4	T.O. 7	F.I. 4	B.D. 3	D. 0	T.U. 8

Observations ended at 72 hours—piece white dry.

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Sample No. 5.

At end of						
24 hours' drying..	B.O. 19	T.O. 12	F.O. 12	B.D. 25	D. 6	T.U. 19
36 hours' drying..	B.O. 17	T.O. 12	F.O. 10	B.D. 19	D. 6	T.U. 15
48 hours' drying..	B.O. 12	T.O. 10	F.O. 6	B.D. 12	D. 6	T.U. 12
60 hours' drying..	B.O. 10	T.O. 8	F.O. 0	B.D. 8	D. 3	T.U. 10
72 hours' drying..	B.O. 6	T.O. 6	F.I. 3	B.D. 3	D. 0	T.U. 6

Observations ended at 72 hours—piece white dry.

In sample No. 3, the line "X" varied in vertical direction but very little from a straight line, at any time. At the last observation it deflected 4/100 of an inch upward at the middle.

In Samples No. 4 and No. 5, the line "X" varied practically none vertically from a straight line.

At the end of 24 hours' drying the pieces had obtained 2/3 of their total shrinkage, in the next 12 hours they obtained 1/4 of their total shrinkage, and all had ceased shrinking at the end of 48 hours of drying.

The ends getting their shrinkage earlier, caused the pieces to bulge in all directions—up in the center and out at the sides. As the drying progressed this bulging decreased but in most cases the lines did not come back absolutely true, while the face in each case came back and even went below a perfectly true line.

Such pieces as these must be dried slowly or the drying of the ends retarded.

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THE CLAY DEPOSITS OF WASHINGTON.[1]

By S. GEIJSBEEK, Portland, Ore.

The "Evergreen State," as Washington is called, has been little known so far as its clay-working industries are concerned. The value of its clay products has increased to such an extent, however, that the clay-working industry forms, at present, an important part in the development of the state resources, and a general description of the clay deposits of the state should materially help the future development of the industry in this particular line.

The value of the clay products manufactured in 1899 was $591,277 and in 1909, $3,060,468, which is an increase of 418 per cent. in ten years. In 1908 the total value was $2,104,289, and the increase for the one year was over 45 per cent. While the clay industry is still in its infancy, it has made, therefore, some remarkable strides, and to-day nearly every kind of clay product, with the exception of the finer classes of pottery ware, is manufactured in the state.

The statistics compiled by the United States Geological Survey of the clay products manufactured in the state of Washington during the year 1910 are not available at the present writing, but for 1909 they are as follows:

Brick:	
Common	$1,081,579
Vitrified	..... [1]
Front	155,600
Fire	103,531
Draintile	18,495
Sewerpipe	737,847
Architectural terra cotta	206,324

[1] Since the writer handed the title of the above article into the American Ceramic Society, a book entitled "The Clays of the State of Washington," by Solon Shedd, Assistant State Geologist and Professor of Geology of the State College of Washington, at Pullman, has appeared. Prof. Shedd's book uses, in some instances, the same data which I had gathered for use in my article, and presumably from the same sources. However, in view of the fact that I have had the matter in preparation for a long time, and have prepared the article without opportunity to know what Prof. Shedd was doing, I have decided to allow the same to be published, notwithstanding the appearance of the treatment of the same subject by Prof. Shedd.

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Brick:	
Fire proofing	71,067
Pottery: Red earthenware	..... [1]
Stoneware	..... [1]
Miscellaneous	686,043
Total value	$3,060,486

There were 143,189,000 common brick manufactured and the average price per M. was $7.55; the amount of vitrified brick manufactured is not given, but the average price was $18.72 per M. 7,802,000 front and face brick were manufactured and the average price per M. was $19.94.

The number of operating firms reporting to the U. S. Geological Survey and included in these statistics was 65, while in 1908 it was 67. The state ranks twelfth in the list of states as to the total value of production.

GEOLOGY.

The geology of the state has been studied only to a very limited extent, and as far as can be judged from the information at hand, some sections have not been investigated at all.

The geological formation of the state is varied, and while the greater part belongs to the younger ages, rocks of the Archean Age are found in some localities.

Granites of the Archean Age are found in the Mica Mountains, south of Spokane, and in several other places in Eastern Washington. The largest beds of decomposed granites are found in the clay deposits of Mica, the clays being used in the making of firebrick, face brick and sewer pipe.

Some granites are also found in the hills around Clayton, north of Spokane, belonging, no doubt, to the same formation as the mica deposits. The residual clays here are stratified in various colors and are of various thickness.

Granites are also found in the Olympic Mountains, but as yet no residual clays have been found here.

[1] Included in "Miscellaneous."

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Some of the clays found along the western slope of the Cascade Mountains belong to the Cretaceous formation, but the majority of the other clay deposits, which are now being worked, are of the Tertiary or post-Tertiary formations. In some parts of this slope, and especially in the Mount Rainier district, the volcanic action has greatly disarranged the formation, and partly calcined these clay deposits, as, for instance, at Taylor, Clay City and Lagrande, and only in a few places have these clays retained their original plasticity as on the Green River, and Sumas District.

The shales which are being worked at present are mostly found in the post-Tertiary formation. In some localities, the shales are overlapped by the glacial formation, as is well illustrated in the clay bank of the Ballard Brick Co., of Seattle, and of the Everett Brick Co., of Everett. Several shale banks have been opened and are now being worked permanently; others have been prospected, but as they are usually located away from rail and transportation facilities, they are not at present worked.

In Eastern Washington, we find a lava formation which has practically covered the whole section. In some sections this lava formation is decomposed and is used for the making of brick. It varies greatly in thickness and texture. Along the streams it is greatly more decomposed than in the high terrace lands, and as the country along the streams is more settled than the inlands, the majority of the brickyards are located along the streams.

The glacial formations are very widely distributed and are being worked extensively. All the clays used in the making of common brick in the Puget Sound section belong to this formation. These clays are characteristically of a blue color and are commonly called "Blue Clays" or "Blue Hard Pan." Owing to the fact that these clays are more or less intermixed with gravel and other foreign substances, they have never given very satisfactory results in the manufacturing of such products as drain and partition tile.

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GENERAL LOCATIONS OF CLAY DEPOSITS

To describe the deposits we will [illegible] two sections, Eastern and Western Washington [illegible] the Cascade Mountain range is the [illegible] section will be divided again into districts.

Western Washington has at present [illegible] clay-working establishments than Eastern [illegible] More clays of the better class, however, are [illegible] Washington, and [illegible] the eastern [illegible] will have the larger clay-working industries.

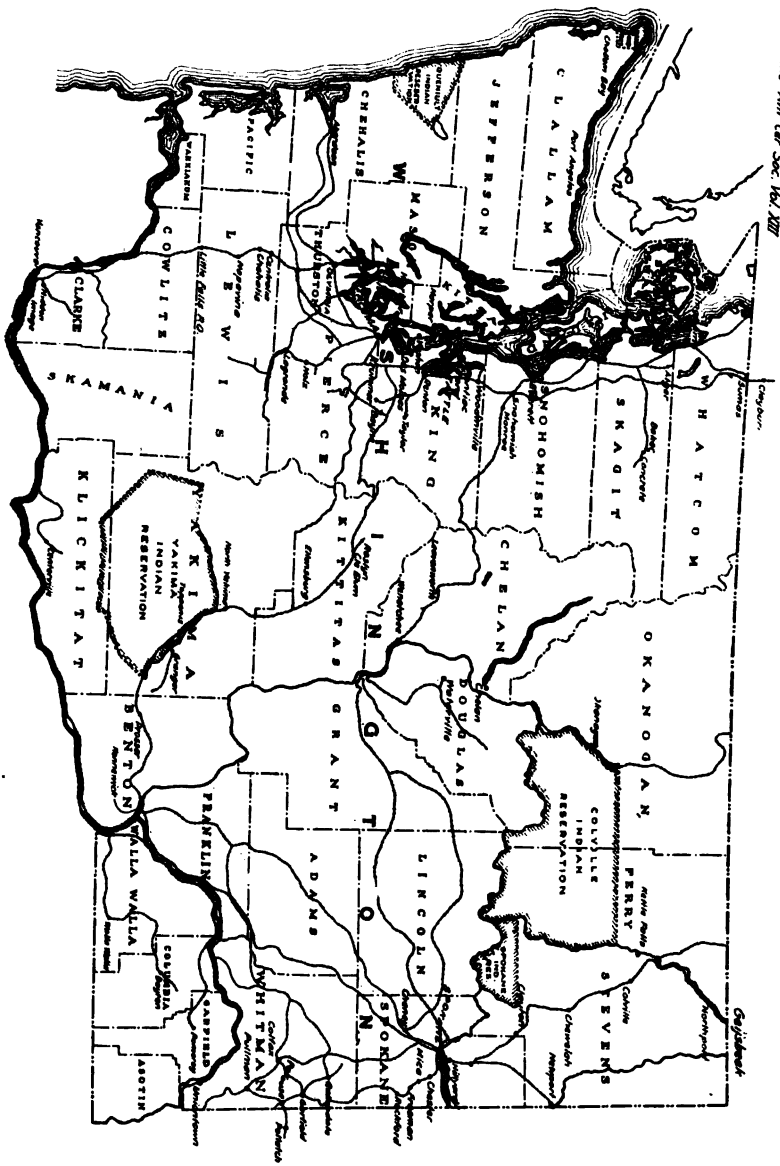
WESTERN WASHINGTON

Northern District.—The northern [illegible] in the northwestern part of the state [illegible] the international boundary on the [illegible] County line on the south and from the [illegible] and the Puget Sound on the west [illegible] Cascades on the east and embraces the [illegible] Skagit, Snohomish, San Juan and Island.

Glacial clays are found in the [illegible] district, while Tertiary clays [illegible] part. The common glacial [illegible] Bellingham and Everett. They are [illegible] and produce a [illegible] Bros. of Bellingham are [illegible] Bellingham while the Day Clay [illegible] [illegible] formation.

The Bellingham Brick and Tile [illegible] [illegible]

[illegible]



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GENERAL LOCATIONS OF CLAY DEPOSITS.

To describe the deposits we will divide the state into two sections, Eastern and Western Washington, of which the Cascade Mountain range is the dividing line. Each section will be divided again into districts.

Western Washington has at present a larger percentage of clay-working establishments than Eastern Washington. More clays of the better class, however, are found in Eastern Washington, and ultimately the eastern part of the state will have the larger clay-working industries.

WESTERN WASHINGTON.

Northern District.—The northern district is situated in the northwestern part of the state and extends from the international boundary on the north to the King County line on the south and from the Strait of Georgia and the Puget Sound on the west to the summit of the Cascades on the east and embraces the counties of Whatcom, Skagit, Snohomish, San Juan and Island.

Glacial clays are found in the western part of this district, while Tertiary clays form the deposits of the eastern part. The common glacial brick clays are worked near Bellingham and Everett. They are free from gravel and produce a good grade of common brick. The Miller Bros., of Bellingham, are operating on the outskirts of Bellingham, while the Day Clay Co. is located some distance from town. Both banks show the same glacial blue clay formation.

The Bellingham Brick and Tile Co. is operating a clay bank at Alger, twelve miles south of Bellingham. This bank has a large amount of surface clay overlying the blue clay, both being used in the making of common brick. The Snohomish Brick Co., of Snohomish, is using a blue glacial clay.

There are two brickyards in Everett. The Schafer Brick Co. is operating on a clay which is part shale and part blue clay. This blue glacial clay, near Everett,

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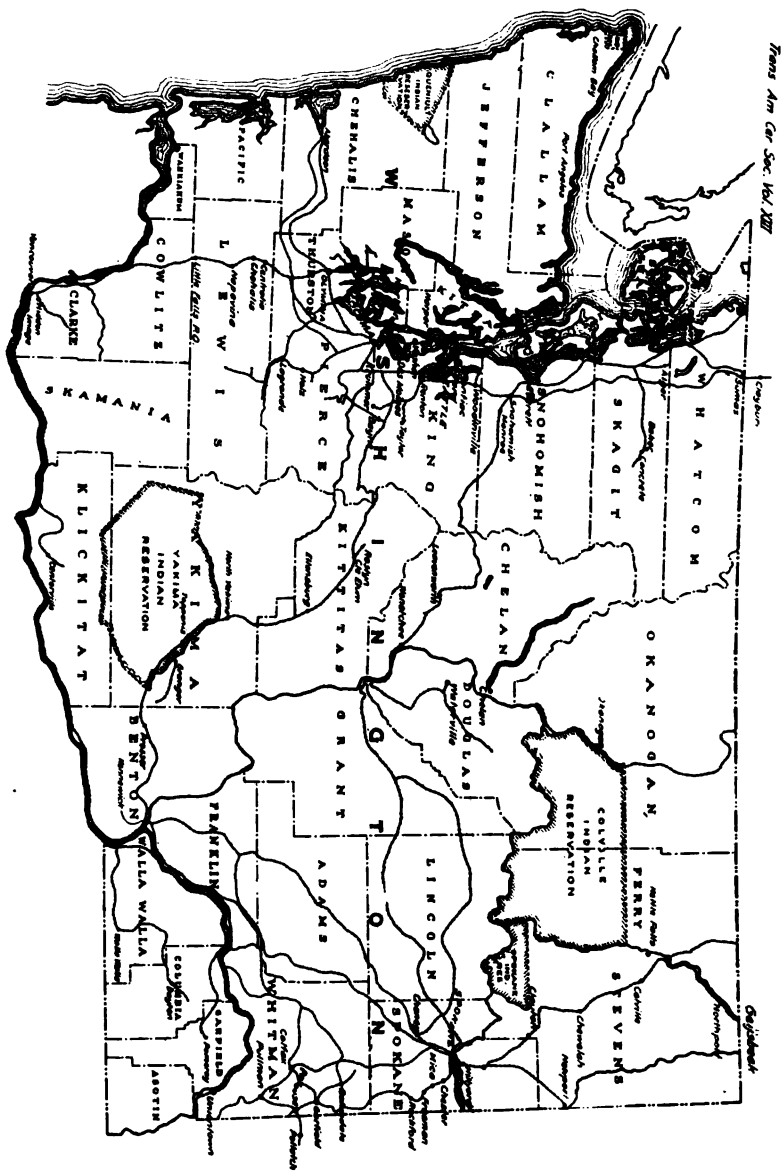

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has also been used on a very small scale in the making of flower pots.

Shales are found near Baker, on the Baker River, at Concrete, on the Skagit River, and at Monroe, on the Snohomish River. At the first two named places these shales are used for cement manufacturing only, while clay at Monroe is not being worked.

Several good deposits of shale are found on the islands in the Strait of Georgia, but they have never been worked to any extent. Common brick was at one time made on Orcas Island.

Blue glacial formations of clay are found along the shores of Whidbey Island in the Puget Sound, while shales and an intermixture of shales and blue clay are found inland on this island. None of these deposits have been worked.

Large deposits of the better grade of clays are found near Sumas on the international boundary line. These clays belong to the Sumas formation and are a part of the Sumas Mountain range. These clays extend well into British Columbia, in fact, the greater part of the clays so far found are on the north side of the boundary line. They are worked extensively at Clayburn, B. C., near the Frazir River. They are used there for the manufacturing of buff, gray and red face brick and firebrick.

The Sumas Firebrick Co. has worked some clays found near Sumas. The color of these clays, when burned, ranges from a yellow-buff to a white. The fire clays found here have shown excellent fire-resisting qualities.

Western District.—This district embraces the counties of Clallam, Jefferson, Chehalis, Kitsap, Mason and Thurston, starting with the Strait of Juan de Fuca on the north, the county lines of Pacific and Lewis Counties on the south, the Pacific Ocean on the west and the Puget Sound and the Pierce County line on the east.

While this section has a large territory, it has not been investigated to any extent, and very few clays have been found and worked except along the shore lines of the Puget

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Sound. The common brick clays are all of glacial formation. The Harper Hill Brick Co., of Harper, is operating a very large clay bank at Harper. The clay is of glacial formation and quite free from foreign substances. The clay here has been worked very extensively for years in the making of common brick.

The Port Orchard Brick Co. is working the same blue glacial formation for common brick. Some bricks have been made by Charles George, of Port Angeles, from these glacial clays.

There are several deposits located in Thurston county but so far only those at Olympia have been worked or used for the making of any clay products, and here common brick were made.

The Olympic Mountains belong to the older ages, and, no doubt, valuable deposits of the better grade of clays will be found in their foothills. Some shales have been mined with coal at Clallam Bay, but this clay has not as yet been used in manufacture of brick.

Southern District.—Bounded by the western district on the north, the Columbia River to the south, the Pacific Ocean on the west, and the Cascade range on the east, the southern district embraces the counties of Pacific, Wahkiakum, Lewis, Cowlitz, Clark and Skamania. This district promises to be a very large clay-working field. Most of the clays so far found in this district are either shales or red-burning plastic clays of the Tertiary Age.

Lewis County has several deposits of good clay, which have been opened up to a very large extent. The Little Falls Fire Clay Co., of Tacoma, is operating a large deposit of clay at Sopenah, near the Cowlitz River, where they have their sewer pipe plant. The clay is found in pockets, and varies in color from red to yellow and white. In some places the clay shows a distinct decomposed boulder formation. These clays are mixed and used for the manufacture of sewer pipe, drain tile and partition tile.

The Chehalis Brick and Tile Co. is using a shale clay found in the hillside close to the plant. They are manu-

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facturing common brick and drain tile. This shale is also found in connection with coal.

The two brickyards which are located in Centralia are both using surface clays, making a fair common brick. There are several localities in Lewis County in which good clays have been found, and ultimately they will be worked. Near Napavine, on the Northern Pacific, is found a very plastic clay, which burns from red buff to yellow. There are several more deposits located in this same locality.

Along the Columbia River, in Clark County, one very large deposit is being worked at Image, four miles east of Vancouver, by the Diamond Brick Co., of Portland. There are several indications of good clay in the southern part of this county. There are several brickyards located in and around Vancouver which are making common brick from the river deposits in the low lands.

Eastern District.—This district contains the counties of King and Pierce, and furnishes the largest amount of clay-working industries in the whole state. Nearly all of the brickyards are using blue glacial clays. The Hill Brick Co., the Builders Brick Co. and the Seattle Brick and Tile Co., are working the clays of Beacon Hill, while the Lohse Brick Co., the Abrahamson Brick Co. and the Washington Brick and Tile Co. are using the clays of West Seattle. The Pontiac Brick Co., located on the Lake Washington side of Seattle, and the Ballard Brick Co., on the Puget Sound, above Seattle, are working large deposits of a mixture of shale and glacial clay for the manufacturing of common brick. The Steele & Steele Brick and Tile Co. are operating a bank on Vashon Island, which is very free of foreign substances. They have been making common brick and also some partition tile. The Woodenville Brick and Tile Co. are operating on Lake Washington, and using a glacial clay deposit. The Lake Union Brick Co. has just opened a deposit of blue glacial clay on the west shore of Lake Union.

All the brickyards around Tacoma are working glacial deposits. The Goss Brick Co. is working the clays of

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the Point Defiance section, while the Gig Harbor Brick Co. is working a deposit on the opposite side of Point Defiance. The Tacoma Trading Company is operating a yard on the glacial clays of Fox Island. Clay of this same formation has been worked to a limited extent at Des Moines and at Edgewood.

The shales in this district have been worked extensively at Renton and are used by the Denny Renton Clay and Coal Co., of Seattle, in the manufacture of paving, sewer and face brick. At Kummer and at Taylor this same company is mining shales from their coal mines for the manufacture of sewer pipe and partition tile.

The coal mines of this district, along the western slope of the Cascade Mountains, and especially the ones of the Carbonado region, have more or less shale in connection with their coal. Some of these shales have been used for sewer pipe manufacturing. At Bayne a deposit of this nature is now being worked to a great extent. The Little Falls Fire Clay Co., of Tacoma, which is operating this plant, are making common brick of this clay for the present, but their intention is to ultimately make paving brick. The shales of this coal-mining district will form one of the most substantial clay-working assets of the state.

The clays of the Cretaceous formation are worked at Taylor, Lagrande, Clay City, Green River and Kummer. At Taylor, the Cretaceous clays are greatly disturbed by volcanic action and are partially calcined. These clays are used by the Denny Renton Clay and Coal Co. for the manufacture of face and fire brick. At Clay City, The Far West Clay Co., of Tacoma, has opened two different deposits. The plastic deposit shows a variety of colored mixtures, red, yellow and white predominating. These clays are used for the manufacturing of fireproofing and partition tile. This clay will stand a high temperature. The other deposit is of a semi-calcined nature and is used for the manufacture of fire brick. The deposits at La Grande show a decomposed boulder formation and have

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been used by the Denny-Renton Clay and Coal Co. for the manufacture of architectural terra cotta.

The clay deposits of the Green River district are not worked to any great extent at present. The best clay found in this section is the high-grade fire clay found on the Hammer property. The clays of the Brooks farm have been used by the Pacific Stoneware Co., of Portland, Oregon, in their stoneware body. The clay deposits of the Northern Clay Co. show a plastic yellow clay in one deposit, while the other deposit is of a sandy nature. The clays of the Griswold farm have been investigated quite considerably and proven to be of quite varied character. These deposits of the Green River section will be worked when better transportation facilities are provided.

At Kummer we find a peculiar formation of a high-grade flint fire clay which is mined by the Denny Renton Clay and Coal Co. in connection with their coal and shale.

EASTERN WASHINGTON.

Northern District.—The nothern district of Eastern Washington includes the counties of Okanogan, Chelan and Douglas. Like most of Eastern Washington, this district is covered, for the greater part, with decomposed lava formation. There is only one brickyard in Okanogan County, but it is making fair brick. In Chelan County, from this decomposed lava, bricks are made on three yards. All these yards are working this same lava formation. Hobson Bros., of Wenatchee, are operating an open pit in which this surface clay has a dirty yellow color. It makes a good soft mud brick. H. A. Durham is working a pit near Chelan, and J. E. Gutherless is operating a small yard near Leavenworth, and A. F. Mafia has a small clay pit at Waterville.

No clays have so far been found in the eastern foothills of the Cascade range of this district.

Western District.—The counties of Kittitas, Grande, Yakima, Benton and Klickitat form this district. Many deposits are being worked in this district, but principally

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in the Yakima Valley which runs, for the greater part, through all these counties. At Cle Elem, Wm. Gunther has a small yard, using an open pit, and at Ellensburg there is a larger yard operated by Coble and Crawford on the same formation. The Garrett Bros., of North Yakima, have opened a large deposit of this surface clay and are making good common brick. The Granger Brick and Tile Co. are located at Granger farther down the Yakima Valley. At Prossor, the Prossor Brick Co. is working a deposit of the same nature, as is the Columbia River Clay Co., of Kennewick. All these firms make common brick from this same decomposed lava.

Shales have been mined at Roslyn in connection with the coal, and used in the manufacture of sewer pipe and partition tile by the Diamond Brick Co. No clays of the better quality have been found in this section with the possible exception of Centerville in Klickitat County.

Southern District.—The southern district includes the counties of Adams, Whitman, Franklin, Garfield, Asotin, Columbia and Walla Walla. The northern part of this district has shown all evidences of possessing excellent clay deposits. Near Palouse we find clay deposits which belong to the decomposed granite formation. These deposits exist east of Palouse and extend across the state line into Idaho, and have been opened up at Potlach and Deary. At Palouse these deposits are being worked by the Potlach Brick Co., who at the same time operate a yard at Potlach. Until recently, the clays were also worked by the Palouse Pottery Co. for the manufacture of stoneware. At Deary, the clays are being worked and used in the making of face brick and firebrick.

The decomposed basaltic formations are found throughout this district and form the basis of the common brick manufacturing. John P. Kusler operates a pit at Oakesdale. The Garfield Brick Co. is working the formation at Garfield. Easum Bros. are using the clay of this formation at Colfax, while the Pullman Brick Co. is making brick of this clay at Pullman, and George Herboth has a

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small yard at Uniontown. The Pommery Brickyard is working a small deposit at that place, while the Dayton Brick Co. is making brick from this basaltic formation at Dayton. At Walla Walla the same formation is used by the Walla Walla Brick and Tile Co., and by the State Penitentiary.

Eastern District.—The largest clay deposits in Eastern Washington are being worked in this district, which embraces the counties of Perry, Stevens, Lincoln and Spokane. The surface lava clays form the greater part of the clays used in making common brick. The better class of clays are found in Stevens and Spokane Counties, and are used in the manufacture of face brick, sewer pipe, partition tile, firebrick, architectural terra cotta and stoneware.

Along the Columbia and Collville Rivers in the nothern part of this district are several places where good common brick clays are found; at Northport, Kettle Falls, Colville and Chewelah.

The Idaho Lime Co. is operating a yard at Newport, close to Idaho line, and is using a decomposed basaltic formation.

Around Spokane, the Dishman Brick Co., the J. T. Davie Brick Co. and the Houston Brick Co. are making common brick from surface lava clay.

At Freeman we find a clay formation which is partly formed by the decomposition of basaltic rocks and granites. These clays are sedimentary and are used by the Washington Brick, Lime and Sewerpipe Co., of Spokane, for the manufacturing of common brick. A deposit is worked close to Chester by the Bergman Clay Manufacturing Co., which is similar to the Freeman deposit except that the basaltic formation is not so evident. These clays run from a yellow to a gray, and are used by this company in the making of sewer pipe, common brick and face brick. At Rockford, a deposit of similar nature has been worked by the Rockford Pressed Brick Co. The Cheney Brick and Tile Mfg. Co., of Cheney, is working a deposit of decomposed basaltic clay.

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Large deposits of the better grades of clays are found at Clayton. These deposits are decomposed granites, which are stratified in various colors. The beds appear in pockets, and are quite deep in thickness. They cover a large area and are used by the Washington Brick, Lime and Sewerpipe Co., at their Clayton plant, for the manufacture of face brick, firebrick and architectural terra cotta. The Spokane Stoneware Co. is using a clay, located about four miles from Clayton, in the manufacture of stoneware and flower pots.

The oldest formation of clay deposits in the state are found at Mica. All of these clays have their origin in the Mica Mountains, being decomposed granites, but which are not as intermixed with various colors as some of the other decomposed granite formation found in other parts of the state. The American Firebrick Co., of Spokane, is working three deposits: one is of a white color and used for the manufacturing of white face brick and firebrick; the largest deposit is used in the manufacture of sewer pipe and partition tile; while the third deposit has a distinct red color and is used for the making of red brick. The Washington Brick and Lime and Sewerpipe Co. has just opened a large deposit at Mica, which they are using for the making of sewer pipe. This deposit has a well marked stratified formation, and has some basaltic formation mixed with the decomposed granites.

	I	II	III	IV	V	VI	VII	VIII	IX	X
Silica	58.96	58.40	63.08	69.50	73.50	64.34	65.66	58.06	40.37	72.68
Alumina	17.72	19.57	17.26	16.36	19.15	20.78	21.98	29.04	38.57	13.15
Iron oxide	6.10	5.20	4.63	4.53	0.65	1.58	1.92	1.82	3.43	2.01
Lime	2.37	4.66	1.32	0.95	0.98	0.68	....	0.62	0.67	0.59
Magnesia	2.96	1.83	1.96	0.47	0.12	0.54	0.90	0.40	0.45	1.21
Alkalies	4.07	3.92	3.98	2.25	2.40	3.66	0.80	1.75	0.08	1.75
Combined water	7.94	6.45	7.64	6.35	3.50	8.63	8.34	8.74	16.86	8.49
Total	100.12	100.03	99.87	100.41	100.30	100.21	99.60	100.43	100.43	99.88

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I.—Glacial clay from Seattle.
II.—Glacial clay from Gig Harbor.
III.—Shale clay from Renton.
IV.—Purple clay from Taylor.
V.—Yellow clay from Taylor.
VI.—Stoneware clay from Green River.
VII.—Stoneware clay from Clayton.
VIII.—Brick clay from Clayton.
IX.—Flint clay from Kummer.
X.—Sewerpipe clay from Mica.

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EXPERIMENTS ON THE DRYING OF CERTAIN TERTIARY CLAYS.

By Edward Orton, Jr., Columbus, O.

Occurrence and Distribution of the Clays.—In the northwestern portion of the United States and Canada, a broad belt of country east of the Rocky Mountains is covered with strata which we are told represent the Cretaceous, Tertiary and later geological periods. As a rule, the Rocky Mountain uplift has brought up igneous or very ancient sedimentary rocks as the back-bone of this great series of ranges; the younger strata are spread in horizontal sheets over the plains country to the east and in some places to the west of the mountains, but their upturned and tilted edges are exposed along the edge of the uplifted area. There it can be shown that they are of very considerable thickness, but away from the mountains, it is seldom that more than a few hundred feet are exposed in any single section.

These strata are composed quite largely of soft friable sandstones, sandy shales, and stratified clays. There are frequent veins of lignitic coal underlain with yellow burning clays, analogous to the fireclays of the carboniferous strata of the central states. The formations are thus seen to include all of the usual types of stratified or fossil clays. In addition, they contain in places a clay-like mineral of very distinct attributes, to which the name Bentonite has been given, and which must be counted as a part of the clay assets of the formations. The general characteristics above described are not intended to apply exclusively to strata of Tertiary Age, but to the Cretaceous also.

Lack of Other Clays in the District.—Beside the stratified shales and fireclays of the Cretaceous and Tertiary Periods, there is little available clay material. The plain or plateau country is, as a rule, covered deeply with a blanket of glacial till, bequeathed by the vast continental glaciers which, in the Ice Age, covered the entire area in

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question. This till is of low economic value here, as elsewhere. It is full of boulders; lenses of gravel and sand are common, and the clay portion is variable over wide ranges of composition and much impregnated with limestone pebbles. Occasional pockets representing some ancient marsh or lake bottom are found which are free from limestone or boulders, making workable beds for common brick and drain tile, but by no chance is anything of better quality likely to originate in these glacial clays. Besides the glacial till, the river valleys which have been cut through the till and into the subjacent bedded rocks are floored on their flood-plains with relatively thin and unimportant beds of fluvial sediments. These river bottom clays are generally very sandy and silty, and at their best are not likely to make superior common bricks. As a source of better clays, they are not to be considered at all.

Thus it appears that over an area of hundreds of thousands of square miles, comprising the plains and plateaus of Wyoming, Montana, the Dakotas, Saskatchewan, and Alberta, the clay supply immediately available is either glacial till or silty river bed deposits—neither of good quality for even common purposes, usually. Where a fault block has been thrust up so as to create a scarp, or where the rivers have cut cañons, the stratified shales and fireclays of the Cretaceous and Tertiary formations are exposed. These occurrences, while insignificant as to area, are nevertheless considerable in actual extent, and are not uncommon all through the territory under discussion.

If this district is to manufacture its own paving brick, sewer pipe, face brick, roofing tile, fire brick, stoneware pottery or terra cotta, it must do so from these occasional occurrences of stratified shales and fireclays. If it cannot do so, then these products must be hauled from the East from 500 to 1500 miles, or from the West from 600 to 1000 miles across the mountain ranges. It is evident that the incentive to use this material is strong and must con-

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stantly grow stronger as time passes, and the country grows in population and needs.

Quality of the Tertiary Clays.—There have been frequent attempts to use these stratified clays for the above purposes. Up to the present time but little success has been attained. The difficulty in general has been due to an inordinate stickiness or adhesive quality in the clays when made plastic, accompanied with large changes of volume in drying and very severe cracking. The cracking forms a kind of network on the surface of the clay mass, resembling the crazing of a glaze. These cracks are shallow at first, but later get deeper until the body sometimes falls in pieces.

The qualities developed by burning these clays is said to be good, or at the least distinctly promising for the production of vitrified wares. Their use would, therefore, appear to hang upon the discovery of some way to overcome their drying difficulties.

THE PRESENT INVESTIGATION.

The data upon which this paper is written was obtained in the study of a group of clays representing either late Cretaceous or early Tertiary formations and being fairly representative of the clay resources of a considerable area in the district previously indicated. As the work was commercial in its origin and objects, it will not be proper to more closely indicate the locality from which the samples were obtained.

Twelve samples were taken, each representing an outcrop of shale or fireclay. These samples were put through the usual preliminary test comprising:

(*a*) Mineral nature, rock structure, or state of aggregation.

(*b*) Observations on grinding properties.

(*c*) Observations on plasticity and working properties when tempered.

(*d*) Shrinkage in drying and observation of drying behavior.

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(*e*) Burning behavior as evidenced by
- (1) Oxidation behavior.
- (2) Color changes at Cones 07, 04, 02, 1, 3, 5 and 7.
- (3) Fire shrinkage at same stages of burning.
- (4) Hardness and character of body developed at each stage.
- (5) Absorption at each stage.
- (6) Overfire behavior.

(*f*) Final conclusions of value of clay, based upon above data.

Without reproducing the data in full, the following summary of the shrinkage changes is important:

Table I.

Clay No.	Nature of sample	Maximum drying shrinkage	Maximum fire shrinkage	Maximum total shrinkage
11	Shales	7.5	7.0	14.5
15		8.4	5.8	14.2
10		12.1	5.9	18.0
13		8.3	6.3	14.6
14		9.4	5.3	14.7
17	Fireclays	8.5	5.5	14.0
21		7.3	5.7	13.0
16		7.3	8.0	15.3
18		10.1	7.4	17.5
20		9.7	6.3	16.0
12	Weathered surface	11.9	6.6	18.5

Based upon the foregoing table, and the other evidence obtained, the following conclusions were drawn upon these samples:

First, that the above 12 samples, as a class, possess an abnormal and sticky type of plasticity, which makes them adhere strongly to metals and other die materials and thus makes them very hard to work or fashion into wares by the usual processes.

Second, that they show an abnormal shrinkage in drying, accompanied by strong warping, twisting and crack-

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ing tendencies, even when made up into small laboratory test pieces, which, in full-sized commercial wares, would result in entirely prohibitory losses.

Third, that on burning they show shrinkages in firing of only moderate amounts, entirely within working limits.

Fourth, that the color, hardness, structural strength, vitrification, etc., developed on proper burning, are in the main very excellent. They are not perhaps as fully desirable as the analogous clays of the carboniferous formations of some other localities, but they are entirely capable of satisfactory use and, in a district far distant from other sources of supply, they would meet all requirements.

The successful use of these materials, therefore, hangs upon the discovery of some means of overcoming the sticky quality when in the plastic state, and the inordinate shrinkage and cracking in drying. Inasmuch as the clays all seemed to participate to a greater or less degree in these objectionable peculiarities, no further work was put upon the study of each individual clay, and the whole study was directed towards finding a treatment which would cure the defects of the clays as a group.

Three compound samples were now prepared by mixing the residues of the samples together. Mixture A contained four shales of similar nature. Mixture B was composed of three buff-burning fireclays coming from immediately beneath seams of lignite coal. Mixture C was also composed of under-clays to lignite seams, but they were impure and red-burning and did not resemble fireclays.

Outline of Tests Tried.—The various modes of correcting abnormal shrinkage, cracking, drying and sticky plasticity, known to the writer, are three:

First, use of anti-plastic bodies, like sand, grog, sawdust, etc., which would reduce the stickiness and reduce the shrinkage, therefore tending to stop the cracking.

Second, use of chemical coagulants, like carbonate of soda, caustic soda, sulphuric acid, tannic acid (from straw), etc.

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Third, use of heat, to break down the organic or inorganic bodies which tend to make the clay impermeable to water, and therefore to give rise to drying troubles.

EFFECT OF ANTI-PLASTIC ADDITIONS.

Experiment 1. Use of Sand.—Mixtures A and B were mixed, respectively, with 50 per cent. river sand, which had previously been passed through a sieve of about 16 meshes per lineal inch. The stickiness was reduced by this mixture, but not overcome. The paste obtained was still sticky and adhesive if wet enough to work well, and crumbly and weak if a little less water was used. At no stage were the working properties good. No smaller additions than 50 per cent. were tried, for this large quantity still failed to correct the stickiness.

Experiment 2. Use of Grog.—Raw portions of Mixtures A and B were mixed with 50 per cent. of the same clays calcined. The calcination had been carried up to a point where the clays had become permanently non-plastic, but the grog differed from sand in being porous and softer, and more likely to form a bond with the plastic clay.

The effect of this addition was not dissimilar to the preceding. It effected some improvement, but did not overcome the stickiness. No smaller quantities than 50 per cent. were tried, because 50 per cent. had failed and still larger additions were impracticable on account of the weakness and crumbling nature of the product.

Experiment 3. Use of Sawdust.—Sawdust is an available substance in large quantities and at low prices in many places in the Northwest. Besides its ordinary anti-plastic effect, there was thought to be some probability of its exerting a chemical action through the tannic acid of the bark and other organic acids or alkaloids of the wood itself. In order to get it into condition to coat well with clay and bond with it, the sawdust was steeped in water until well saturated. The sawdust was previously passed through a sieve of 8–10 mesh per lineal inch to remove coarse particles. Mixture A was mixed in two propor-

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tions by weight, *viz.*, 5 per cent. and 10 per cent., and also with two other proportions by volume, *viz.*, one-half bulk sawdust to one bulk clay, and one bulk sawdust to one bulk clay. Mixture B was mixed with 10 per cent. sawdust for one trial and bulk for bulk for another trial.

In order to get data of more practical value, the trial pieces were made up in full brick size. The drying was carried out in three ways:

First, a quick drier operating at 85° C. for 24 hours.

Second, a medium drier—operating at 50° C. for 72 hours.

Third, a slow drier—operating at 20° C. (room temperature) for a week.

The same drier comparisons had been made for the Geological Survey of Ohio upon 68 Ohio clays, comprising shales, fireclays, surface clays, with the following results:

15 per cent. of clays tested stood the 85° 24-hour treatment.

66 per cent. of clays tested stood the 50° 72-hour treatment.

85 per cent. of clays tested stood the 20° 7-day treatment.

Thus it is seen that the methods used upon the clays in question were not more severe than the clays of Ohio were usually able to meet successfully.

The bricks of Experiments 1, 2 and 3 were exposed to the three ways of drying and the results were negative in all cases. None of the mixtures would stand either the 85° drier nor the 50° drier, nor the 20° open-air treatment. All cracked, but Experiments 1 and 2 were better than No. 3, and the cracking at 20° was not bad.

The bricks in all of these cases dried rapidly on the shell or surface, while the interior still retained its water as a rubber-like paste. The exterior naturally cracked in attempting to shrink down on the unshrunken core. Only when the exterior cracks opened avenues into the interior for the water to escape did the interior make rapid progress towards drying.

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These experiments show that the cause of the drying trouble is the peculiar quality of the *impermeability* of the plastic clay. Ordinary clays are more or less granular and water flows through their capillaries with ease. But the clays under test seem to permit water to move through the mass with extreme difficulty, nor is the presence of sand or grog, or sawdust, of much assistance in opening up the pore system. The plastic paste envelops these grains of foreign matter, but is not itself changed thereby, and as long as the clay constitutes an encompassing paste or matrix, the situation cannot change much. If enough anti-plastic were used to actually create gaps or holes in the plastic encompassing paste, it might help in the drying, but the mixture would be so gritty as to be unworkable anyhow, and hence nothing would be gained.

The use of anti-plastic was, therefore, abandoned with too little beneficial results in their use to justify further experimenting.

USE OF CHEMICAL COAGULANTS.

It is a widely discussed belief that many clays contain substances thought to be organic, but thought by some to be inorganic, but in either case to be jelly-like or glue-like. These bodies are known as colloids, being the reverse of crystalloids. Much has been written about them in recent years and many things attributed to their influence which is in excess of what can be proved.

The researches of Ashley and others have shown that different clays in which the so-called colloidal ingredients are high are affected in marked ways by the addition of chemicals which coagulate and render denser these bodies. Striking experimental evidence of this has been produced. Very recently the same reasoning has been applied to certain problems of impermeability of soils, with promising results.[1]

[1] K. F. Kellerman, Science, page 189, February 3, 1911.

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In the present investigation four different coagulants were tried:

Experiment 4. Use of Caustic Soda.—Only Mixture A was tested. To two portions of one pound each, one gram and two grams were added, respectively. This amounts to 0.2 and 0.4 per cent., respectively. The mass was tempered up, molded into a brick and dried slowly. The results were not improved in any way.

Experiment 5. Use of Carbonate of Soda.—To Mixture A 0.2 and 0.4 per cent. of carbonate of soda was added, as before. No good result followed on drying.

Experiment 6. Use of Sulphuric Acid.—To Mixture A 0.6 per cent. of strong sulphuric acid (1.8 sp. gr.) was added, and the mass tempered, molded and dried. The results could be noticed—there were fewer cracks, but larger ones, than in the untreated clay. The treatment did not seem promising and would have bad effects upon the color and working and burning behavior of the clay in any case.

Experiment 7. Tannic Acid.—Acheson[1] has shown that tannin, gallo-tannic acid, catechu, extract of oak bark, extract of sumac, infusion of oat straw, etc., produce remarkable physical alterations in some clays, increasing their tensile strength, and improving their drying qualities. He has also suggested that the use of straw by the ancient brick-makers, as mentioned in Holy writ, was for the tannic acid effect, rather than for the more obvious reason of increasing the tensile strength by use of a fibrous material.

In order to test this, straw was cut up into short fibers, from 1/4 to 1/2 inch long, and introduced into Mixtures A and B in the following proportions each, *viz.*, 2.5 per cent., 5 per cent., and also by bulk in proportions of 1 clay to 1/2 straw, and 1 clay to 1 straw. On tempering and drying there was absolutely no beneficial effect. The cracks in the samples most highly charged with straw

[1] Trans. A. C. S., Vol. VI, p. 31.

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were just as bad as ever, though the straw did impart ability to hang together better after the piece was cracked clear through.

There seems no advantage attainable either from the chemical effects of the tannin or other colloids of the straw nor from its use as a fibrous anti-plastic.

The chemicals employed comprise those which have been used in other connections, with notable results on the state of agglomeration of clays. In clay casting in potteries in particular, carbonate of soda is widely used to coagulate the slips but its effects here has been practically nil.

USE OF HEAT TO FLOCCULATE THE CLAY.

Professor A. V. Bleininger, working first at the University of Illinois,[1] and later at the Bureau of Standards,[2] has developed an important method of treating clays which stubbornly crack in drying, by heating them up to temperatures varying from 200° C. to 350° C. (he mentions 400° C. as being tried by a friend, in one instance). He explained the change produced on the basis that the organic or inorganic colloids are shriveled up and rendered either temporarily or permanently unable to take up water, and assume their former jelly-like condition. While in this flocculated state, they let water pass freely through the mass as it does in any normal plastic clay paste, and thus they may dry safely and with much diminished shrinkage. Professor Bleininger has suggested the use of the rotary kiln for calcining clays which need this pre-heating treatment.

This work of Bleininger's seems the most promising method thus far advanced for dealing with clays of this type. It was, therefore, made the subject of careful test.

[1] Trans. Am. Cer. Soc., Vol. XI, p. 354, 392; *Ibid.*, Vol. XII, p. 504.
[2] Bull. Bureau of Standards, Vol. VII, Part 2, p. 143.

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Experiment 8. First Pre-Heating Test.—Samples of the Mixtures A, B and C, sufficient to make full-sized bricks, were placed in drying ovens and were heated to 100° C. (212° F.), 150° C. (500° F.), and 200° C. (390° F.), for 6 hours. Another sample of each was placed in a gas-fired muffle kiln and heated for 6 hours at 300° C. (570° F.). These various samples were now made up and their drying behavior tested. Neither the treatment of 100° C. (212° F.), 150° C. (300° F.), or 200° C. (390° F.) made an appreciable difference in the behavior of any of the mixtures.

In the sample heated to 300° C. (570° F.) there was a distinct improvement. The clay no longer felt so sticky when tempered with water. It worked shorter and more granular and the drying was improved, though by no means corrected.

Experiment 9. Second Pre-Heating Test.—In order to get the benefit of more accurately controlled conditions, a large brick test kiln was heated up to 330° C. (625° F.), and a sample of Mixtures A, B and C was placed inside in a fireclay box or tray and exposed for 90 minutes. Other samples were given the same treatment for 120 minutes. The temperature was carefully controlled all the time by an electric pyrometer.

In a similar way, other samples were exposed in the same kiln to a temperature of 400° C. (750° F.) for 30, 60, 90 and 120 minutes, respectively.

Another batch was then heated to 450° C (840° F.) for 30 minutes. These three treatments produced a distinctly noticeable change in color of the clay mixtures. They changed from their initial yellowish gray or bluish-gray to brownish tones, and in the 450° C. (840° F.) sample, to a light reddish color, indicating the near approach of the changing point of the clay produced in regular burning.

The clays were now made up into bricks and dried. There was a distinct change, but not a consistent or regular one. Some samples dried safe at one point and cracked

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again when tried a second time or when fired at a heat which should have still further improved their behavior. Others still cracked under all rates of drying, but in a distinctly less aggravated degree.

Experiment 10. Third Preheating Test.—The preceding trials had already covered the ground described by Bleininger in his experiments and gone to a far higher temperature than he had employed, without curing the troubles. There has been no improvement worth mentioning in the lower temperatures and only by going to temperatures which he had indicated as excessive had any really encouraging gains been made. The discouraging feature was that the gains were so irregular and inconsistent.

The mechanical difficulty of heating clay in large quantities to an accurately controllable temperature above 300° C. (570° F.) without the aid of motion to prevent local overheating or underheating is apparent. Bleininger recognized this in recommending the rotary kiln. It seemed probable that the spotty and irregular character of the results obtained at 400° C. (750° F.) and 450° C. (840° F.) were due to portions of the clay having been exposed more completely than other portions to the heat, and the corresponding incompleteness of the reaction or chemical change.

Accordingly, a miniature rotary kiln was devised out of a piece of wrought iron pipe of about 4 inches diameter by 30 inches long. This was heated over a gas fire, making a kind of muffle over and around it, the two ends sticking out to the open air. The temperature in this tube was regulated by an electrical pyrometer, the thermo-couple of which was in the center of the tube, in contact with the moving clay. The clay was fed in at one end and the tube, which was slightly inclined, was slowly rotated by hand power, and the clay fell further and further down the tube till it finally fell out into a receptacle at the lower end.

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Three runs were made with this apparatus: The first was at 480° C. (900° F.), in which the clay passing through was exposed 10 minutes to the heat. The second was at 580° to 625° C. (1075 to 1150° F.) and lasted 18 minutes. The third was at 470° to 490° C. (880 to 920° F.) and lasted 35 minutes. The ends sought by this treatment were only partially gained by them, for the clay fed down too rapidly at times and the temperature fluctuated widely in spite of the greatest care. The clay which had passed through was irregular in color. Some grains were light cream, or pink, others black, etc., indicating unequal burning.

These three sets of conditions were applied to Mixtures A, B and C with results which, though far from satisfactory, gave encouragement to persist. The B mixture, composed of buff-burning fireclays, was very definitely improved, while the Mixture C (red-burning fireclays) was somewhat improved and the Mixture A (shales) was cracking still, though much diminished in degree and with a very different kind of cracking from its initial behavior.

So far as could be observed, the difficulties of securing a full or equal treatment of all parts of the material were not yet overcome by the rotary tube and the inconsistencies of the results were probably due to this cause. To still further clinch this point, the following experiment was made:

Experiment 11. Mixing Preheated Clay in Different Proportions.—In a commercial rotary kiln, it would be possible that the material delivered would be like that coming from the little tube described in Experiment 10, *viz.*, there would be over-done, correctly fired, and underdone material mixed together. To more accurately understand the effect of this, batches of Mixtures A and B were prepared, composed of:

	Per cent.
Calcined clay (completely dehydrated).....	25
Preheated to 400° C. for 90 minutes.....	50
Preheated to 335° C. for 90 minutes.....	25
	100

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Bricks were molded from these mixtures and dried in the usual way. Mixture A cracked badly. Mixture B slightly. This seems to indicate that the *entire mass of the clay must be heated for the right time at the right temperature*. Over-burning one part does not make up for underheating another part.

Experiment 12.—Without any very well defined idea, a shallow fireclay tray 1.5 inches deep was filled with clay from Mixture A, and placed for 2 or 3 hours in the ordinary gas stove by which the laboratory was heated. The weather was not very cold, and the fire was not burning very strongly, but the clay was at a temperature but shortly below redness for several hours. When removed, it had changed to a flesh color, and when wet with water it developed but little plasticity at first. On grinding with water, however, it speedily became plastic enough for good working purposes. A brick made from this material, laid upon a warm stove top dried in 3 or 4 hours without a flaw.

This remarkable result occasioned great surprise and renewed courage, for the drying test was very severe and the preheating treatment equally so, so far as could be judged. It seemed to point to the importance of continuity of heat treatment and a new effort was made in that direction.

Experiment 13. Second Rotary Kiln.—A new rotary kiln was made of 18 gauge sheet iron having a diameter of 15 inches by length of 9 inches. This cylinder had 4 holes, 3 inches in diameter, in each head, for free influx of air. It was heated in an improvised furnace, in which the temperature could be kept fairly constant by means of a thermo-couple inserted through the hollow axis of the cylinder. The shell of the cylinder was dull red in passing over the zone and cooler, of course, on the balance of the way around. The clay lay on the bottom in the hot zone, but was not visibly red hot itself.

In this cylinder, the entire batch of clay to be treated was introduced and kept until it had been heated through and through. Rotation by hand kept the mass changing

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position all the time, but not escaping from the heat. The temperature of the clay probably ranged from 450° to 510° C. (840 to 940° F.) during the latter part of the treatment, after the clay had become fully heated through and through. There was a very perceptible burning out of carbon from the clays. This was evidenced by their change in color, and by the sparkles and dull glow on the clay as the drum slowly revolved.

It seemed that the best way to get results with this apparatus was by running it at a fixed temperature (as above) and varying the duration of the treatment with the different clay mixtures.

The following data were secured by use of this apparatus:

Mixture A.

Heated a 450°–510° C. in Rotary Drum.

Duration of treatment	30 min.	45 min.	60 min.	60 min. duplicate
Color	Black	Yellow	Yellow	Yellow
Plasticity	Good	Good	Fair	Fair
Drying at 50° C.	Bad	Better	Good	Good
Drying at 85° C.	....	.....	.....	Bad
Drying in open room ...	....	Bad	.....	.....

It must be borne in mind that very few clays will stand the 85° C. drier (in Ohio, only 15 per cent. of clays treated will stand it) so that failure of Mixture A to stand this test is not to be wondered at.

Mixture B.

Heated at 450°–510° in Rotary Drum.

Duration of treatment	25 min.	30 min.	45 min.
Color	Black	Black	Black
Plasticity	Short	Short	None
Drying at 50° C.	Good	Good	.....
Drying at 85° C.	Bad	Bad	.....

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The 45-minute sample was non-plastic and no brick could be made from it. This swift change from the 30-minute treatment seems to show that the treatment must be pretty accurately controlled.

Mixture C.

Heated at 450°–510° C. in Rotary Drum.

Duration of treatment	30 min.	45 min.	50 min.
Color	Yellow	Yellow	Yellow
Plasticity	Good	Fair	Short
Drying at 50° C.	Bad	Very slight	Good
Drying at 85° C.	.....	Bad	Bad

A difference of 5 minutes in the treatment seems capable of producing marked difference in the results.

Summary on the Preheating Data.—The foregoing tests show:

First, that exposure of these clays to temperatures of 100° C., 150° C., 200° C., 300° C., and 330° C. for periods of from 30 minutes to 6 hours gave no important gains—the clays still continued to develop the same peculiarities, rubbery plasticity, and the fine-meshed drying cracks.

Second, that exposure in fireclay trays to temperatures of 400° and 450° C., without stirring, gave evidence of chemical changes and improved drying qualities, though still entirely unworkable from a commercial standpoint.

Third, that exposure for periods of 10, 18 and 35 minutes in a short rotary tube, to temperatures of 480°, 580–620°, and 470–490°, respectively, gave similar evidence of chemical changes and improved drying qualities, but still too irregular and erratic to be commercial.

Fourth, by exposure by chance to unknown conditions, but which must have been of longer duration and higher temperature than those included in paragraphs 1 and 2 gave a perfect result on one clay.

Fifth, that acting on this clue, a rotary drum heated to 450–510° C. gave satisfactory treatments for all sam-

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ples, the duration of the treatment being the critical matter, with apparently a margin of only about 5 minutes in some cases.

Sixth, that so far as can now be seen, it is possible to devise a preheating treatment which will do away with the stickiness of these clays and cure their cracking in drying, but this treatment must be far higher in temperature than anything ever proposed by Bleininger or any one else, and is therefore a matter for still further consideration.

CHANGES PRODUCED BY THE PREHEATING TREATMENT.

The physical evidence of important chemical changes brought about by the preheating treatment are: (1) Change of color; (2) marked change in the nature of the plasticity and entire loss of plasticity if the treatment goes too far; (3) cessation of cracking in drying. In order to more fully understand the changes taking place, samples of unburned Mixture A and the same after subjection to the preheating treatment at 480° in the rotary drum were prepared and analyzed for carbon and chemically-combined water by Prof. D. J. Demorest.

The results are:

Sample	Carbon	Total water	Water expelled at 105° C.	Water expelled at red heat
Raw clay.....	1.81	11.25	7.35	3.90
Same, after preheating at 480° C.	0.09	7.83	4.73	3.10

This analysis gives at once a considerable insight into the situation. From it, the following deductions may be made:

First, the clay appears to be of different mineralogical make-up from the ordinary clays in use elsewhere. Its plastic base is probably not the mineral kaolinite, which is generally considered to be the chief clay-forming aluminum silicate, or at least, it is not that mineral alone. It is probably some other hydrous aluminum silicate, like

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Bentonite, a mineral of higher water content, variously given as 16 to 18 per cent. This mineral occurs frequently in streaks ranging from one inch up to several feet in thickness among the Cretaceous and Tertiary formations of the Northwest, and was seen at several points in collecting the foregoing samples.

The samples collected were greenish or yellowish, becoming nearly white on drying out. It is immensely fine-grained and feels like soap between the teeth, except for occasional grains of sand which are scattered through it. The three following analyses illustrate its chemical peculiarities:

Components	No. 1 sample	No. 2 sample	Rock Creek Wyoming sample
Silica	54.13	68.0	59.78
Alumina	19.67	13.5	15.10
Oxide of iron	4.82	2.3	2.40
Lime	2.08	2.0	0.73
Magnesia	1.86	0.4	4.14
Alkalies	0.40	....	....
Sulphur trioxide	....	0.3	....
Carbon dioxide	0.51	....	....
Water	16.50	13.0	16.26
Totals	99.96	99.5	98.41

The first and second samples came from the district represented by this investigation. The Rock Creek sample is quoted from Ries "Clays, Their Occurrence, Properties and Uses", 2nd Edition, page 513). In the first analysis, the water and the dehydrated material were for some reason reported separately, and have been recalculated into one analysis by the writer.

Since Bentonite was observed to be present in streaks in these formations, it certainly lends color to the suggestion that it may occur throughout the clays and shales, lending to them its peculiar physical characteristics. Bentonite is a

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material of excessive water-absorbing capacity. It works up into a mucilaginous paste, using 3 or 4 times as much water as a kaolinitic clay would do and swelling greatly in volume. This paste dries with great shrinkage and inordinate cracking.

All of the fireclays and shales examined consist to a considerable degree of ordinary quartz sand, as do most other clays. It is necessary to assume, therefore, that the aluminous silicate which furnishes the plastic element of these samples must have contained a larger amount of easily expelled water than any ordinary kaolinitic clay, for the samples tested in this case were dry and dusty when weighed out, and still showed the very high water content expelled at 105° C. A clay with kaolinite as its base would not be able to absorb or retain anywhere near the quantity of hygroscopic water that these samples show. One remarkable feature of the case is that the sample which had been preheated to 450°–510° C. showed that it had taken up 4.73 per cent. water after the preheating treatment, while a kaolinite similarly dried would not have taken up more than a per cent. or two.

The discovery of the probable non-kaolinitic character of these Cretaceous and Tertiary clays, if confirmed by more thorough studies, is of great interest from the geological standpoint.

Second, its loss of stickiness and cessation of cracking may be due to two different causes, *viz.*, the burning out of the organic substance or the partial dehydration of the aluminum silicate base of the clay, or to both. The important amount of the change in the water content, and the smaller amount of the carbonaceous matter expelled, make the latter seem less likely to be the active cause of the changed physical properties. The fact that the carbon does burn out just at that time, and that the clay changes color in consequence, is probably a minor or concurrent change and not the one which so profoundly affects the clay's nature. It is impossible to make this or any other statement on this point with confidence, however, as small

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amounts of colloidal matter has been shown by Acheson to have great effect in some cases, and if the carbonaceous matter in this clay really is a colloidal body, instead of merely vegetable mold or lignitic inclusions, it may be the cause of the physical qualities of the clay.

The clays here treated seem to indicate a retention of plasticity after the expulsion of part of the combined water. This phenomenon has been observed before[1] under even severer treatment.

The ability to slake down to a soft mud is not uncommonly shown in clays which have been heated only to low red heat and kept at that temperature for some hours.

PRACTICAL BEARING OF THE PREHEATING DATA.

The question now arises: "*Is the Proposed treatment practical?*" There are several points bearing on this matter which should be understood in reaching a conclusion on this point:

First, the preheating treatment found necessary in these clays is much more severe than that found necessary in any other case on record. It requires a temperature bordering on or actually reaching redness.

Second, the different clays showed that the point at which over-burning and consequent total loss of plasticity occurs is perilously close to the point which must be reached to produce good results. In other words, the heat treatment needed seems a narrow zone of temperature. Below this, the treatment is ineffective, and above it, it spoils the clay very quickly.

Third, this will always make the labor item in preheating the clay somewhat costly because of the necessity for high-grade supervision and fine regulation.

Fourth, Bleininger's suggestion of the rotary kiln is the only one which seems to promise such accurate temperature control as these clays seem to demand. The use of the rotary kiln should not be excessively costly, so far as

[1] R. C. Purdy, Trans. Am. Cer. Soc., Vol. IX, pp. 213–215.

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the interest on the investment and running expenses for power and fuel are concerned. The clays themselves will supply a part of the heat required by the burning out of the carbonaceous matter, and lignitic coals generally occur in connection with the clay strata under discussion.

Fifth, it is highly likely that a period of expensive and costly experimenting would have to be passed through before any plant could be adjusted to give this preheating treatment with the desired accuracy. On the other hand, with money and intelligence, there seems a way opened to make use of these clays in an area where they would be of immense industrial importance.

In the foregoing, no distinctly new contributions to knowledge are claimed. The main facts to be emphasized are: (1) That the Bleininger preheating treatment, to be operative with these clays, must be at temperatures far higher than he used. (2) That a loss of combined water is here recommended as a necessary step in the reduction of the too great adhesiveness in these plastic clays. (3) That the elimination of the hydrocarbons of these clays is coincident with successful treatment, if not a necessary precedent thereto.

DISCUSSION.

Mr. Barringer: I would like to ask how you determined and weighed the carbon.

Mr. Orton: I employed a chemist, Mr. D. F. Demorest, to do the work for me. I warned him that there might be some carbon dioxide in the clay, and if it was there, that he must expel it by a dilute hydrochloric acid treatment, before making a carbon determination. He made his carbon determinations by combustion in oxygen, I believe, weighing the resultant CO_2 in potash bulbs. Regarding the water, I told him I wanted him to determine real water and not loss on ignition, and I have confidence that he did so.

Mr. E. Gates: We did some work on this on the Coast. It was a question between Mr. Moore and myself, after

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treating one of these clays and mixing it, how long a tempered clay body may be allowed to stand before use. That is, if mixed and allowed to stand for a week, whether it would return to its former condition or not.

Mr. Orton: Professor Bleininger has alluded to the fact that the improvement in drying from the preheating is the result of the lag with which water is taken up by the clay, and the difficulty with which water is passed through it before the preheating treatment, and the rapidity with which it was passed through it after treatment. Professor Bleininger concluded, I believe, that the improvement consisted in taking advantage of this lag in water absorption, but that the change in structure was not so drastic as to prevent the clay from ultimately resuming its former character.

I do not think that this explanation will cover the situation disclosed by the figures submitted in my data. There we seem to have produced a change which is permanent. The carbon certainly could not be restored, and I do not think the water content would reassume the former amounts by any amount of wetting and drying out again.

Mr. Bleininger: This paper is exceedingly interesting, and the work that Professor Orton has done in carrying up the temperature as high as he has, was certainly necessary, and I am very glad that he has done it. I think he has proven beautifully the change in the content of the combined water, and it is evident also that the carbon elimination has been of influence on the structure. In how far we can lay the difficulty in working to the carbon itself, is a problem. It has been a great pleasure to hear Prof. Orton's paper.

Mr. Orton: We have heated some of the clay up to temperatures as great as those at which this actual decarbonization was effected, and yet not kept the treatment up long enough to get the change in color. Where we did not get the change in color, we did not get the beneficial results. It appears that the carbon must be expelled in order to get the desired result. It may be that the carbon is

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merely acting as an indicator, and that the change which really does the work is the loss in water in the base of the clay. That point will have to be proven before it can be accepted.

We find that if we take a portion of the clay, correctly treated, and mix with it a portion of clay which is *under-treated*, and a portion of clay which has been *over-treated*, *i. e.*, heated to a still higher temperature, but still not burned clear of the carbon, that we get back into drying troubles again at once. It seems that only a small amount of clay in which the dark color still exists may be present without occasioning cracking trouble.

Mr. Lovejoy: We are up against the same problem, and we hope the thing will be carried out commercially some time within the year. We found in a particular case that we could dry the stuff successfully by mixing the dehydrated clay with the raw clay in percentages of half and half. We do not know how much lower than this we can go—this being the limit of our experiment.

Mr. Barringer: What do you mean by dehydrated clay?

Mr. Lovejoy: Unfortunately, I do not know the percentage of dehydration. We instructed our clients to put enough clay for a commercial test of top of an up-draft kiln while it was cooling. How much dehydration they got, I do not know. They reported that the bricks went through the drying and burning safely, and the resulting product was very satisfactory. Just before I left, we got the results of the laboratory tests previously mentioned, and we dried the wares successfully from a mixture of raw clay with dehydrated clay, so we have not only the laboratory test but also a practical yard test.

Mr. Barringer: Do you mean in the laboratory test that you mixed the raw and dehydrated, and that the dehydrated clay was actually dehydrated?

Mr. Lovejoy: I do not know to what extent it was dehydrated. I simply know the clay that was put through that particular heating treatment and carried up to the

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highest temperatures we have been using in these tests, and given time, we probably went beyond the temperatures that we had in those original treatments, and perhaps above the temperatures that we had in the rotaries, probably more fully dehydrated than any of these. But the dehydration was sufficient to overcome the trouble with the raw clay so that it seems likely that by completely dehydrating the clay we can overcome the trouble. I know in one instance in the report of this same material it was said that by mixing grog with it to the extent of 50 per cent. it could be dried safely. The grog in that case was made from different material.

Mr. Orton: Thoroughly dehydrated?

Mr. Lovejoy: Thoroughly dehydrated, so that addition of grog seems to overcome the trouble. The addition of sand had little effect. We made a practical test of the clay alone and the bricks cracked like a war map before we could get them into the drier. They even cracked on the cutting table. In five minutes after the bricks came from the cutter, they would be completely covered with cracks. We mixed the clay with 30 per cent. sand and it helped to the extent that we could get the bricks from the machine to the drier, but in fifteen minutes the bricks containing sand were as bad as the raw clay bricks, so that the mixture of sand did not help much.

Mr. Bleininger: The reason we did not go higher with our clay was that most of our clays became grog-like in character and were no longer sufficiently plastic. All of our clays, therefore, were treated at these lower temperatures. We observed in each and every case that the color of the clay changed. That probably is due to the iron itself as very likely the carbon is not eliminated, at least at the lower temperatures.

Mr. W. D. Gates: Something over twenty-five years ago, we were using a red clay that we were grinding. Every bit was wet and we had to dry it. We constructed a series of coils on which we heated the clay until it developed a reddish tinge. It was then ground and placed in bins. In

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later years we found out why we had been successful with our clay handled in that way, but we did not know at the time.

Mr. Keele: Professor Orton's paper is of peculiar interest to me, because just now we are struggling with similar difficulties in clays, which occur over a large area of the Canadian Northwest.

Although our shales or clays that cracked while drying were mostly from Tertiary strata, we also found, in two instances, shales from the Cretaceous coal measures, which behaved quite as badly in this respect.

Owing to the pressure due to greater depth at which the latter occur and the folding and faulting which the whole formation has undergone, it might reasonably be expected that these causes would result in a partial dehydration of the clay or shale, or at least tend to destroy the colloid matter in them.

These two Cretaceous shales, however, were exceedingly plastic and sticky when wet, and cracked as quickly, after being set to dry, as any of the Tertiary clays.

In the experiments undertaken to deal with these drying defects, we also tried various substances, and found that 1 to 2 per cent. of hydrochloric acid added to the mixing water, or 1 per cent. of common salt added to the clay, would generally cure the worst cases of cracking.

The clays treated in this way would not stand fast drying, but would dry in the ordinary room temperatures without checking.

There was a slight efflorescence on some of the test pieces after drying, but some clays did not show this at all. The fire tests are not advanced enough yet to show how the burned ware will be affected by the addition of salt.

In the preheating experiments, some of the clays had to be heated to 500° C. before they could be dried after wet moulding.

Mr. Knote: As to adding salt to the clay, I tried a very brief experiment on that. My idea was to add

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some salt or sodium carbonate to the clay, which scummed very badly, and in several trials the scum was materially reduced and had a slight glaze on the surface. I think the gentleman will find that his trials come out in that way.

Mr. Barringer: It seems to me that there is certainly a real trouble from all the evidence we have had, and that some such treatment as has been outlined will probably be necessary. Mr. Lovejoy, do you think it would be practical to employ the waste heat of kilns in accomplishing the partial dehydration of clays as suggested?

Mr. Lovejoy: I doubt if we can get sufficient temperature from waste heat to overcome the trouble, and I also doubt if we can control the temperature sufficiently to get satisfactory results.

When you consider that we must reach a temperature between 400° C. and 500° C.—almost red heat—and that this temperature must be maintained day and night, the use of waste heat from our kilns, either that of combustion or cooling, is very questionable.

We must control the temperature within a limited degree—how limited we do not know—but we must destroy enough plasticity to make the ware safe drying and at the same time retain enough to form the ware.

Our dehydration problem resembles the old Bessemer converter problem of oxidation.

If the limits within which we must work are close, and if, further, complete dehydration of a portion of the clay will accomplish the same purpose, it seems to us that the latter method is the most practical, and for this work waste heat would not be adequate except perhaps the waste heat from combustion.

We can readily maintain the temperature required for complete dehydration in a direct fired rotary drier, and the cost would not be prohibitive, especially in the district under discussion, where fuel is close at hand and where the price of common bricks will readily stand the expense.

Clays can be dried in a rotary drier at a nominal expense, and the heating up of the clay after it is dry will be

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but a slight addition to the cost, since the specific heat of clay is only about one-fifth that of water.

If the problem can be solved by completely dehydrating a portion of the clay, and mixing with raw clay, the solution is quite simple.

The dehydration could be done either in rotary kilns or in vertical kilns such as are used for calcining. We have a wide range from complete dehydration to sintering within which we may work.

Mr. Bleininger: The rotary drier in any case would have to be operated at a red heat, since the rate of passage would determine the temperature of the clay.

Some years ago, I made a study of this question, and from what I know of the operation of clay driers, it should not be a very difficult problem, especially since nowadays they are beginning to operate them with mechanical stokers. In the experiments made at Pittsburg it was found that we could maintain the same temperature for days in a mechanical stoker furnace with a very reasonable degree of accuracy, using very ordinary help. Care was taken in these experiments to employ men who had no training, who knew very little about mechanical stokers.

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SOME OBSERVATIONS ON THE QUALITIES OF PAVING BRICKS.

By EDWARD ORTON, JR., Columbus, Ohio.

In the autumn of 1909, the National Paving Brick Manufacturers' Association[1] caused an investigation of the rattler test as applied to paving bricks to be made, with intent to discover the causes of the wide discrepancies found between the results obtained by different engineers and brick testers. The rattler test, as set forth in specifications by the National Brick Manufacturers' Association in 1901, had been in use 8 years or more without any substantial alteration, but at no time since the adoption of the test had it been usual to find close concordance between different laboratories when testing the same material, and these differences in some cases were so great as to impair the confidence of both manufacturers and consumers in the value of the test. The convenience of the rattler test, its already wide adoption, its demand for the same qualities which are demanded by street wear, all united to make its retention of importance.

The failure to check was attributable to the laxity of the original specifications, which permitted the use of variously designed machines, differing even in details of construction in the revolving barrel itself, as well as giving too wide discretion in the matter of speed of rotation, renewals, physical properties of shots, constitution of charge, weighing of fragments, etc. The new effort was to be directed to the removal of this laxity, and to so tie down the operators that if they followed the rules of the test, they could not vary in result, except in so far as the material itself varies.

In February, 1910, the writer, learning of this investigation, proposed to the officers of this Association to cooperate with them in carrying the study through. The idea advanced was to make all studies in duplicate, in two

[1] Not to be confused with the National Brick Manufacturers' Association, which is an entirely different body.

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different laboratories, and then, by exchange of data, find and eliminate the causes of variation. This proposal involved the entire independence of each laboratory, each to pay its own costs, except that the machine for making the tests, and the samples to be tested, should be furnished by the Association. This proposal was accepted and a long and costly investigation made. Mr. Marion W. Blair was appointed by the Association to take charge of their portion of the work and continued in charge to the end. The writer desires at this point to acknowledge his indebtedness to Mr. Blair for many suggestions during the course of the work.

In planning the investigation to be made, the primary object was to define the rattler test as a test, and eliminate its causes of variation, but a secondary object entered in, *viz.*, to study paving bricks as such, and learn what degree of variability to expect in the material and from what causes it comes. The results of the first part of the study, with improved specifications for the rattler test, have been transmitted to another organization.[1]

The results of the second part are presented herewith. In preparing this second study, the writer has used the data obtained from his own laboratory only. An equal amount of work was done by Mr. Blair in his laboratory, and this data could have been included in this study had it been deemed desirable. To have done so would have doubled the mass of data without altering the conclusions here reached.

LINES OF STUDY UNDERTAKEN.

The following lines of study were taken up:

First, what differences in mean rattling strength should be expected in first-class paving bricks due to the position of the sample in the kiln?

Second, in first-class paving bricks of the same make,

[1] American Society for Testing Materials, Vol. XI. Joint paper by Marion W. Blair and Edward Orton, Jr.

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and which have had the same burning treatment, what variation in rattling strength should be expected from structural differences and concealed defects?

Third, among different brands of paving bricks having a reputation for good quality and which have been in use for 10 years or more in the streets of many cities, what variation may be expected in their ability to withstand the rattler test?

NATURE AND RESULTS OF THE EXPERIMENTS PERFORMED.

Four samples, designated successively Series A, E, F and G, consisting of 2100 bricks each, were selected by Mr. Blair. In each case these were taken from one kiln at the factory where made, and seven hundred of each sample were chosen to represent the upper third of the kiln, seven hundred to represent the middle third and the remaining seven hundred the lower third of the kiln. These respective portions were taken from a compact block or area of apparently uniform hardness and the samples were chosen to represent the best material in their respective levels of the kiln.

Each large sample was then marked, loaded into a car and shipped at full car rates, to avoid danger of mixing in handling. One-half of each lot of each bench was taken at one laboratory and the balance went to the other. Each laboratory, therefore, received 350 bricks from each bench of each sample, or 1050 in all.

On receipt of these samples, they were housed, or placed in roofed piles, to prevent their becoming or remaining more than "air damp." From each lot of 350 bricks, 100 were taken at random, dried in a kiln 24 hours at a temperature not exceeding 200° C. nor less than 100° C., cooled, marked with numbers in white paint, weighed to the nearest one-hundredth of a pound, soaked in water for 48 hours, wiped and reweighed, the difference taken and per cent. absorbed calculated. The wet bricks were then dried out in the kiln as before, for 24 hours.

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The absorption per cents. were then arranged in column form, in order of numerical value. The ten highest were grouped together, and the ten lowest. The remaining eighty were then grouped in eight groups, so selected that every charge contained an assortment of bricks of which the average was within one or two hundredths per cent. of every other charge. Two sample charges are shown herewith, to illustrate.

Table I.

Absorption Per Cents.

No. of brick	Charge 1.	Charge 2
1	0.33	0.32
2	0.42	0.42
3	0.59	0.52
4	0.62	0.62
5	0.82	0.83
6	0.92	0.92
7	1.00	1.04
8	1.12	1.18
9	1.43	1.43
10	1.62	1.43
Average	0.88	0.87

These eight charges were then divided into two lots of four each, to each of which one of the two extra charges was given. One lot contained 4 average charges and the charge of highest absorption out of the one hundred bricks under classification, and the other lot contained four average charges and the charge of lowest absorption. One lot was given the rattler test with cubic shot and the other with spherical shot.

From the remaining 250 bricks of each lot, 100 more were taken and divided up into 10 charges at random. These 10 charges were then rattled, 5 with the cubic shot and 5 with spherical shot.

From the remaining 150 bricks, 75 more were taken and divided into 5 charges of 15 each, and these were

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rattled with no shot at all. The remaining 75 bricks were held back for extras, if needed.

The rattler tests were thus made with cubic shot, spherical shot, and no shot, upon ungraded bricks, and with cubic shot and spherical shot upon bricks graded by the absorption test. This was done for all three benches of each kiln. The following scheme shows more clearly the plan of work:

Table II.

			No. of charges	No. of bricks per charge	Total No of bricks for each set of tests
Top zone	Cubic shot	Air-dry, ungraded	5	10	50
		Graded by absorption	5	10	50
	Spherical shot	Air-dry, ungraded	5	10	50
		Graded by absorption	5	10	50
	Without shot	Ungraded by absorption	5	15	75
Middle zone	Cubic shot	Air-dry, ungraded	5	10	50
		Graded by absorption	5	10	50
	Spherical shot	Air-dry, ungraded	5	10	50
		Graded by absorption	5	10	50
	Without shot	Ungraded by absorption	5	15	75
Lower zone	Cubic sho.	Air-dry, ungraded	5	10	50
		Graded by absorption	5	10	50
	Spherical shot	Air-dry, ungraded	5	10	50
		Graded by absorption	5	10	50
	Without shot	Ungraded by absorption	5	15	75
Totals			75		825
Reserve supply of bricks to each investigator for his own use and for checking					225
Total bricks required per sample for each laboratory					1050

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The rattler tests were the standard test of the N. B. M. A. in the case of the cubic shot, and in the spherical shot tests, the only intentional variation was in the substitution of $1\frac{7}{8}$-inch spheres for the $1\frac{1}{2}$-inch cubes, and $3\frac{3}{4}$-inch spheres for the $2\frac{1}{2} \times 2\frac{1}{2} \times 4\frac{1}{2}$ parallelograms. In each class, the weights of the small-sized and large-sized shots were the same. All the other conditions of each test were kept as nearly identical as possible. In part of Series A and E, a new variety of stave was tried as noted in the foot-notes. In Series C, also a new set of staves of the original type was used:

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Table III. Series A.

Lower Bench.

Charges graded by absorption					Charges ungraded by absorption		
	Cubic shot	Absorption, per cent.	Spherical shot	Absorption, per cent.	Cubic[1] shot	Spherical[1] shot	No shot
	18.57	1.24	20.64	1.25	20.86	22.58	26.21
	18.84	1.25	20.19	1.22	22.05	23.23	25.23
	18.18	1.25	21.26	1.25	18.86	24.14	25.32
	16.87	1.24	20.08	1.24	20.18	24.06	22.98
	17.92	0.58	22.69	3.39	21.84	23.68	25.85
Av.	18.07		20.97		20.76	23.54	25.12
Middle Bench.							
	17.76	1.01	17.96	1.03	18.08	22.05	24.84
	16.15	1.01	18.03	1.00	18.74	22.52	22.32
	15.93	1.01	19.15	0.99	19.30	23.28	21.58
	15.24	1.01	17.22	1.01	18.30	21.01	23.07
	18.71	1.66	18.25	0.58	20.42	20.92	24.44
Av.	16.65		18.12		18.97	21.95	23.25
Upper bench.							
	17.89	1.75	17.74	1.75	20.48	23.41	22.27
	16.20	1.75	19.12	1.75	18.36	22.84	21.88
	18.41	1.75	19.28	1.75	21.53	22.28	23.55
	18.14	1.75	19.25	1.75	19.47	25.17	23.02
	20.68	3.01	17.03	0.91	20.12	23.33	22.61
Av.	18.28		18.48		19.99	23.40	22.65

[1] The 15 tests in these columns were made with the old form of channel steel staves, in badly distorted condition from warpage. The other tests of this series were made with a lined channel steel stave in good condition. Comparisons cannot be drawn between different columns, and only between the different tests of one column at a time.

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Table IV. Series E.

Lower bench.

Charges graded by absorption					Charges ungraded by absorption		
	Cubic shot.	Absorption, per cent.	Spherical shot	Absorption, per cent.	Cubic[1] shot	Spherical[1] shot	No shot
	18.42	2.91	20.19	2.91	19.54	24.63	25.80
	18.73	2.92	20.87	2.91	20.43	22.53	26.14
	17.80	2.92	20.33	2.91	19.19	24.44	26.66
	18.59	2.91	20.15	2.91	21.97	22.97	24.78
	16.55	0.96	22.70	4.41	19.62	23.24	25.22
Av.	18.01		20.85		20.15	23.56	25.72

Middle Bench.

	15.36	1.22	18.81	1.23	18.31	19.18	23.11
	15.49	1.20	19.31	1.23	18.43	22.16	22.74
	15.98	1.21	18.52	1.21	17.03	21.58	23.51
	17.36	1.21	18.96	1.21	19.64	21.34	23.27
	18.88	3.24	16.84	0.55	18.57	20.97	23.14
Av.	16.61		18.49		18.34	21.06	23.15

Upper Bench.

	16.78	0.94	17.54	0.94	15.72	16.86	21.42
	16.74	0.94	17.72	0.94	16.79	18.59	20.96
	15.33	0.94	17.34	0.94	14.41	17.85	21.46
	16.32	0.94	17.58	0.94	16.24	17.88	22.65
	17.45	1.84	16.11	0.55	16.31	17.64	19.83
Av.	16.57		17.26		15.85	17.76	21.26

[1] The 10 tests represented by the Lower and Middle benches of these columns were made with the old form of channel steel staves, in badly distorted condition from warpage. The other tests, representing the Upper bench in the columns, and the other three columns complete, were made with a lined channel steel stave in good condition. Comparisons can only be drawn between the different tests in one column, and in this instance not quite a complete column is comparable.

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Table V. Series F.

Lower Bench.

Charges graded by absorption					Charges ungraded by absorption		
	Cubic shot	Absorption, per cent.	Spherical shot	Absorption, per cent.	Cubic shot	Spherical shot	No shot
	14.67	1.35	17.74	1.38	15.82	21.46	22.19
	16.27	1.37	19.30	1.39	16.38	20.58	22.46
	16.75	1.39	19.20	1.40	15.29	20,18	22.77
	17.72	1.39	20.63	1.36	16.36	22.22	22.73
	18.80	0.67	19.21	1.88	18.77	18.87	23.26
Av.	16.84		19.21		16.52	20.66	22.68

Middle Bench.

	14.88	0.82	19.18	0.82	16.61	19.73	21.62
	16.24	0.81	17.81	0.81	16.58	20.08	21.93
	16.50	0.82	19.02	0.84	16.94	19.60	19.80
	15.36	0.82	18.70	0.82	15.83	19.00	19.00
	14.61	0.30	20.75	1.44	17.50	20.81	20.23
Av.	15.52		19.09		16.69	19.84	20.51

Upper Bench.

	18.90	0.88	22.04	0.88	18.16	20.00	23.55
	16.86	0.87	23.75	0.92	18.59	20.80	25.23
	17.65	0.93	19.69	0.89	20.40	22.55	24.61
	18.59	0.91	20.28	0.89	19.88	20.20	22.49
	19.51	1.86	18.28	0.26	16.66	21.71	25.11
Av.	18.30		20.81		18.74	21.05	24.19

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Table VI. Series G.

Lower Bench.

	Charges graded by absorption per cent.				Charges ungraded by absorption		
	Cubic shot	Absorption per cent.	Spherical shot	Absorption per cent.	Cubic shot	Spherical shot	No shot
	15.63	1.00	19.82	1.00	16.81	19.91	23.93
	16.27	0.98	19.30	1.01	17.23	19.06	22.61
	16.92	0.98	21.12	1.01	17.08	19.08	21.88
	16.83	0.98	19.67	1.02	17.34	21.02	22.36
	16.35	1.40	21.69	0.36	19.44	20.05	22.93
Av.	16.40		20.32		17.58	19.82	22.74
			Middle Bench.				
	17.35	1.16	20.72	1.14	16.60	19.71	22.05
	17.87	1.15	21.25	1.14	17.47	23.13	23.96
	17.96	1.14	21.85	1.16	18.83	21.19	25.04
	17.78	1.15	20.39	1.15	17.65	20.76	23.12
	17.96	0.49	29.70	2.48	18.56	22.05	24.13
Av.	17.78		22.78		17.82	21.36	23.69
			Upper Bench.				
	18.87	1.56	22.06	1.58	16.74	22.02	24.19
	18.76	1.57	21.49	1.58	17.43	22.10	24.36
	17.29	1.55	21.51	1.56	17.55	22.55	24.45
	17.64	1.55	21.20	1.58	16.72	22.60	24.42
	20.77	2.42	21.60	0.94	17.25	22.31	24.23
Av.	18.66		21.57		17.14	22.31	24.33

In addition to the above four series, another sample, designated Series C, selected exactly as before, was tested in like manner, except that the grading of the 100 bricks by absorption was abandoned, and a new set of staves was used, of the same variety as used in the four preceding series.

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Table VII. Series C.

Lower Bench.

Cubic shot	Spherical shot	No shot
22.96	22.53	26.17
21.84	23.23	27.73
21.94	22.86	27.12
20.74	21.14	27.57
22.90	22.36	27.76
21.46	22.60	
21.87	23.81	
20.40	21.86	
21.51	23.73	
21.52	23.58	
Average, 21.71	22.76	27.27

Middle Bench.

22.13	24.76	26.66
24.34	22.69	28.91
23.11	23.18	26.29
23.37	22.42	28.46
23.00	24.18	26.91
21.01	20.71	
23.81	23.54	
24.62	21.94	
26.11	22.69	
24.93	21.75	
Average, 23.67	22.79	27.45

Upper Bench.

22.92	21.59	25.75
21.03	22.12	25.77
23.78	21.71	26.09
21.15	22.67	25.72
21.62	22.31	
22.35	22.25	
20.72	23.10	
Average, 21.93	22.25	25.74

Series D. Series D was taken from a loaded car and did not represent grading as to level in the kiln. It merely represented the rejection of seconds and culls, according to the usual visual standards. In place of 2100,

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3000 were taken, giving each operator 1500. These were used without grading by absorption in a series of tests at 10 brick per charge. One point to be determined in these series was the influence of the composition of the iron in the shots. Shots of the spherical shape only were used in making this comparison. Another point upon which evidence was sought was the influence of various types of staves, and in these tests, the shots were kept uniform in quality and shape and the staves were the only variable. Altogether, in this series, 130 charges were tested by each operator using 1300 bricks each. Tables VIII and IX give these data:

Table VIII.

Using shot No. 1	Using shot No. 2	Using shot No. 3	Using shot No. 4	Using shot No. 5
21.06	20.25	21.78	24.25	21.47
23.06	21.50	22.71	23.24	21.70
20.96	22.05	21.47	21.78	22.58
24.31	19.24	22.36	23.20	21.94
23.63	22.96	ä 21.31	24.40	24.43
24.60	22.06	21.91	23.44	21.47
23.37	21.08	20.95	24.29	24.00
22.58	21.49	21.88	24.72	21.80
26.41	22.18	20.79	22.12	22.61
23.63	21.98	19.57	24.60	24.07
Average, 23.37	21.47	21.47	23.60	22.60

Table IX.

Using stave No. 1	Using stave No. 2	Using stave No. 3	Using stave No. 4	Using stave No. 5	Using stave No. 6	Using stave No. 7
21.06	21.40	20.49	20.45	20.37	19.39	20.61
23.06	22.28	22.35	21.72	21.23	19.43	20.13
20.96	21.21	22.13	22.61	20.78	19.47	21.93
24.31	21.57	22.02	22.47	21.81	20.64	21.55
23.63	22.61	22.87	25.12	23.44	21.13	20.43
24.60	23.87	22.22	20.49	20.21	21.41	20.00
23.37	22.05	20.86	22.06	21.15	17.69	20.05
22.58	23.01	21.54	25.12	20.97	21.24	21.25
26.41	25.64	22.16	22.48	20.55	19.65	20.84
23.63	23.30	23.08	22.43	20.76	19.62	19.73
Average, 23.37	22.59	21.97	22.49	21.12	19.96	20.65

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Tentative Standard Series. At the conclusion of these tests, a tentative standard process was formulated, using the information which had been gained as to types of shot and types of staves, and 10 brands of bricks, with 10 charges of each brand, were now run by the proposed process.

The samples used in these 10 comparisons were in part what was left of the Series A, C, E, F and G, together with five new lots, designated as F2, H, K, M and P, respectively. These lots were mostly selected by the manufacturers and represented what they thought was their best material, but it does not represent any special bench in a kiln, nor was it necessarily chosen from any single kiln. Lot F2 was selected from a street delivery. Tables X and XI give these data:

Table X.

Tests Made by the Revised or Tentative Standard Rattler Process.

Series A	Series C	Series E	Series F	Series F2
18.78	23.80	18.55	17.51	17.25
20.06	24.44	18.23	18.44	16.94
20.24	23.95	20.09	18.75	19.27
18.72	24.97	18.08	18.63	17.55
19.47	24.49	19.02	17.99	18.92
19.26		18.83	17.30	16.65
18.96		19.60	17.48	15.86
19.89		20.54	19.51	15.44
20.38		20.87	18.70	15.65
20.12		19.37	17.74	18.46
Average, 19.59	24.33	19.31	18.20	17.19

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Table XI.

	Series G	Series H	Series K	Series M	Series P
	19.14	25.67	20.30	18.41	16.40
	17.90	30.47	18.42	18.08	16.46
	18.45	30.23	17.68	20.36	16.81
	18.24	25.66	19.42	18.40	17.40
	18.60	29.76	18.97	18.78	16.84
	19.58	23.33	17.59	19.64	
	18.53	25.07	20.23	17.24	
	19.35	28.34	18.57	19.25	
	19.13	29.44	18.46	18.38	
	18.81	30.25	19.63	20.20	
Average,	18.77	27.82	18.92	19.07	16.78

The foregoing tables, containing the results of 585 tests, represent that part of the data produced by the writer in the joint investigation. As explained previously, Mr. Blair's portion is not used in this study.

It will also be understood that comparisons between the different kinds of shots, or between different lots of the same shots, or between the different kinds of staves, cannot safely be made in the foregoing, because the conditions governing that portion of the work have not been set forth here. The conditions in any one vertical column of figures are consistent and comparable, except where indicated otherwise, but from column to column, they are not always so. Hence, the only conclusions which should here be drawn are those based on a study of the uniformity of the material, as disclosed by the different sorts of tests applied.

I. INFLUENCE OF POSITION IN THE KILN.

The popular conception of engineers and brick users, and possibly some brick manufacturers also, is that any single brand of paving brick has a characteristic quality inherently its own, and that when a bid to supply paving bricks is made by a brickmaker, and a sample is filed and tested, and a contract is let upon that bid, the brickmaker

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should deliver material which, on test, will show the same figures as the sample submitted. In many cases great injustice has been done to brickmakers by a too literal application of this conception by engineers, directors of public improvements and similar officials.

The general idea outlined above has a foundation of truth. A paving brick clay *does* tend to produce a characteristic product. The product of one clay *is* inherently better or worse than another. Some clays produce brittle, dense, glassy products; others soft, punky products; others hard, stony, tough products; and so on, with innumerable gradations between these types. But the fact to to be borne in mind in this connection is that these inherent or characteristic qualities are much disguised or concealed by two sets of factors—variation in burring treatment, which may or may not have been the best, and variation in structure due to the flow, under pressure, of clay through the die of the brick machine.

In any given clay, the temperature range over which its qualities remain at their best, or close to it, is of the utmost importance. In some few clays this range in heat treatment is quite wide, and but little difference in quality is found from top to bottom of a kiln. In many more, this heat range is rather close, and either a little over or under the best point will show at once on the product and any wide departure will discredit the material at once. In some other clays, the available heat range is so very narrow that the material cannot be worked for vitrified goods profitably at all.

It is of course well recognized that in any kiln there may be zones or areas in which the distribution of the heat is not good, and the product may be either over- or underfired in consequence. The question upon which light is here being sought is to what extent does the quality of paving material vary in kilns that are *well burned*, and which manufacturers would put forward as good? It is not to find out how much un-uniformity one may find in a kiln of paving bricks, by hunting out the hot spots and

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cold spots, but rather how much uniformity may one find under good working conditions?

With this in view, the data presented in Series A, E, F, G and C were analyzed with care. The remaining data gave no evidence on this point.

Table XII.
Averages of Each Series by Benches.
Series A.

Bench of kiln	Graded charges[1]				Ungraded charges[2]		
	Cubic shot		Spherical shot		Cubic shot	Spherical shot	No shot
	Rattler	Absorption	Rattler	Absorption			
Lower	18.11	1.24	20.56	1.24	20.76	23.54	25.12
Middle....	16.27	1.01	18.09	1.01	18.97	21.95	23.25
Upper	17.66	1.75	18.85	1.75	19.99	23.40	22.65

This brick was fired in kilns of the down-draft type. The center of the kiln yields consistently the better ware in four out of five comparisons. This indicates that the upper ware was slightly over-fired, for its absorption per cents. are higher as well as its rattler losses, such as would ensue from a slightly spongy structure. The lower ware is probably higher in rattler losses from a slightly less complete vitrification, as indicated by its slightly higher absorption per cent., though the difference is seemingly trifling. In the case of the no shot charge, the upper bench yields a little better figures than the middle. This may be due to the superior activity of an iron shot charge over brick-on-brick in attacking a spongy exterior structure caused by over-fire, or it may be an accidental figure, caused by one erratic result in an average of only five tests.

[1] Average of 4 tests only. The charges representing the 10 highest and 10 lowest absorptions in 100 bricks were discarded in this comparison.

[2] Average of 5 tests each. Their average absorption cannot possibly vary by more than very small amounts from the averages given in the graded series.

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Table XIII.
Series E.

Bench of kiln	Graded charges[1]				Ungraded charges[2]		
	Cubic shot		Spherical shot		Cubic shot	Spherical shot	No shot
	Rattler	Absorption	Rattler	Absorption			
Lower	18.38	2.92	20.38	2.91	20.15	23.56	25.72
Middle....	16.05	1.21	18.90	1.22	18.34	21.06	23.15
Upper	16.29	0.94	17.54	0.94	15.85[3]	17.76[3]	21.26

This ware was fired in down-draft kilns. It is apparently not over-fired in the upper zone of the kiln, for its absorption per cent. and rattling strength both indicate a slight superiority over the middle, and a decided superiority over the bottom benches. These relations hold in four out of the five comparisons and in the fifth the differences are so small as to be of little significance.

Table XIV.
Series F.

Bench of kiln	Graded charges[4]				Ungraded charges[5]		
	Cubic shot		Spherical shot		Cubic shot	Spherical shot	No shot
	Rattler	Absorption	Rattler	Absorption			
Lower	16.35	1.38	19.22	1.38	16.52	20.66	22.68
Middle....	15.74	0.82	18.68	0.82	16.69	19.84	20.51
Upper	18.00	0.89	21.44	0.89	18.74	21.05	24.19

[1] Averages of 4 tests only. The two charges representing the 10 highest and 10 lowest absorption figures were discarded.

[2] Averages of 5 tests each.

[3] Made with different staves than the two other benches. This magnified the difference somewhat.

[4] Averages of 4 tests only. The two charges representing the 10 highest and 10 lowest absorption figures were discarded.

[5] Averages of 5 tests each.

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In four out of five comparisons, the middle of the kiln yields the best material. In one comparison, the lower bench surpasses the middle by a few hundredths. This material is fired in down-draft kilns and the clay requires a high temperature to bring it to vitrification. Forcing the fires, in order to get the bottom hard enough, results in damage to the upper portion, as is very clearly shown above. The damage, however, is not by production of spongy structure to any serious extent, but comes about from brittleness chiefly.

Table XV.
Series G.

Bench of kiln	Graded charges[1]				Ungraded charges[2]		
	Cubic shot		Spherical shot		Cubic shot	Spherical shot	No shot
	Rattler	Absorption	Rattler	Absorption			
Lower	16.41	0.98	19.98	1.01	17.58	19.82	22.74
Middle....	17.74	1.15	21.05	1.15	17.82	21.36	23.69
Upper	18.14	1.56	21.56	1.57	17.14	22.31	24.33

The ware represented in these tests was fired in a kiln of horizontal draft. The fire holes deliver their heated gases near the floor, and this is illustrated nicely in four out of the five comparisons here made. The top ware in this kiln is the softest ware.

Table XVI.
Series C.

Bench of kiln	Cubic shot	Spherical shot	No shot
	10 charges	10 charges	5 charges
Lower.....	21.71	22.76	27.27
Middle.....	23.67	22.79	27.45
Upper.....	21.93	22.25	25.74

[1] Averages of 4 tests only. The two charges representing the 10 highest and 10 lowest absorption figures were discarded.

[2] Averages of 5 tests.

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No absorption tests were made upon this material. It was burned in down-draft kilns, but did not attain as high a degree of vitrification as most of the preceding samples did. Its top portion is a little better than the middle and lower benches in all three comparisons, only one discordant figure being noted and that for a few hundredths. While the rattling strength of this material is poorer than the preceding, its uniformity from bench to bench is very excellent indeed, and not surpassed by any brand tested.

Summary of Section I.—Judging from these five brands of bricks, representing five factories in different parts of the country, each a successful and prominent one in its district, and representing different varieties of clays and different types of kilns, it is possible for paving brick makers to keep their product within an average fluctuation of 2 to 3 per cents. rattler loss, so far as differences in burning are concerned. Care must be taken that this statement is thoroughly understood. It applies to *averages* only. The fluctuation of bricks in any one zone may greatly exceed this amount, as will be shown in the next section. In considering any small amount of data, the fluctuations of the individual charges are so great as to completely obscure the above relationship. But where averages of 5 or 6 tests of one bench can be compared against an equal quantity from another, the above principle seems to hold quite closely.

It is not believed that the average performance of the average paving brick plant would show as small a fluctuation in its output as two or three per cent. due to variations in their burning treatment, but the instances studied show what is being done among some of the better plants.

II. VARIATION OF BRICKS OF THE SAME HARDNESS, DUE TO STRUCTURAL DEFECTS.

In a bar of clay expressed from a brick machine, a considerable length, say 50 or 100 feet, will probably show all the important peculiarities of bar structure which can occur, at least those due to occur at any single temper of

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the clay. A very soft or extra hard temper might still further vary the character of the output. But if one takes one short length of a clay bar, representing one brick, and compares it with another, cut from a point a little further along in the same bar, the variation between the two may be considerable. One may possess laminations, dry spots, cavities, air blisters, surface cracks, etc., which the other does not show. In fact, no two seem exactly alike.

It follows from this, that in any charge of ten bricks chosen for a rattler test, there is an assortment of somewhat dissimilar units, and this dissimilarity is liable to cause the results to fluctuate rather widely, even when the burning treatment has been all that could be desired.

With a view to finding out what variation in strength, as measured by loss in rattling, good paving bricks of uniform hardness show, the following data have been analyzed out of the tables given in Tables III to XI, inclusive:

The *Range* is obtained by subtracting the minimum result from the maximum of the set. The *Deviation* is obtained by first calculating the mean of the set and then determining the differences between each observation and the mean. The sign of these differences (*i. e.*, whether plus or minus) is ignored. The differences obtained are then averaged, and the figures thus obtained show in the given set of results how much any individual result is likely to deviate from the general average or mean. This term is not necessarily in close agreement with the ange between maximum and minimum, for *one* erratic result may make the latter quite wide, but not greatly affect the average deviation from the mean.

Tables XVII–X XIV give the results of this study:

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Table XVII.
Series A.

Bench in kiln	Cubic shot		Spherical shot		No shot	
	Total ranges	Average deviations	Total ranges	Average deviations	Total ranges	Average deviations
Lower	1.97	0.55	2.61	0.80	3.23	0.83
	3.19	0.99	1.56	0.51		
Middle.....	3.47	1.16	1.93	0.46	3.26	1.11
	2.34	0.71	2.36	0.79		
Upper	4.48	1.02	2.25	0.88	1.67	0.49
	3.17	0.86	2.89	0.71		
Average ...			2.26	0.69		

Table XVIII.
Series C.

Bench in kiln	Cubic shot		Spherical shot		No shot	
	Total ranges	Average deviations	Total ranges	Average deviations	Total ranges	Average deviations
Lower	2.09	0.54	2.22	0.68	1.59	0.50
	1.95	0.71	1.47	0.38		
Middle.....	2.21	0.40	2.34	0.82	1.62	0.99
	5.10	1.35	2.83	0.79		
Upper	1.08	0.34	2.75	1.00	0.55	0.15
Average ...			2.32	0.73		

Table XIX.
Series E.

Bench in kiln	Cubic shot		Spherical shot		No shot	
	Total ranges	Average deviations	Total ranges	Average deviations	Total ranges	Average deviations
Lower	2.18	0.68	2.55	0.75	1.88	0.57
	2.78	0.82	2.10	0.77		
Middle.....	3.52	1.20	2.47	0.66	0.77	0.19
	2.61	0.58	2.98	0.77		
Upper	2.12	0.56	1.61	0.46	2.82	0.69
	2.38	0.71	1.73	0.41		
Average ...			2.24	0.64		

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Table XX.
Series F.

Bench in kiln	Cubic shot		Spherical shot		No shot	
	Total ranges	Average deviations	Total ranges	Average deviations	Total ranges	Average deviations
Lower	4.13	1.13	2.89	0.59	1.07	0.28
	3.48	0.69	3.35	0.96		
Middle.....	1.89	0.68	2.94	0.69	2.93	1.00
	1.67	0.42	1.81	0.48		
Upper	2.65	0.84	4.47	1.45	2.74	0.96
	3.74	1.12	2.55	0.86		
Average....			3.00	0.84		

Table XXI.
Series G.

Bench in kiln	Cubic shot		Spherical shot		No shot	
	Total ranges	Average deviations	Total ranges	Average deviations	Total ranges	Average deviations
Lower	1.29	0.38	2.39	0.87	2.05	0.55
	2.63	0.74	1.96	0.60		
Middle.....	0.61	0.17	9.31[1]	2.56[1]	2.99	0.89
	2.23	0.69	3.42	0.97		
Upper	3.48	0.76	0.86	0.20	0.36	0.09
	0.83	0.32	0.58	0.21		
Average ...			3.09[1]	0.90[1]		

Table XXII.
Series D.

All tests with spherical shot. 10 tests per set.

	Shot No. 1	Shot No. 2	Shot No. 3	Shot No. 4	Shot No. 5
Total range.....	5.45	3.72	3.15	2.94	2.96
Average deviation from mean.....	1.15	0.77	0.65	0.84	0.93

[1] These figures are due to one very erratic result. Excluding this figure, on the presumption that there was something irregular about it, these values would be 1.46, 0.49, 1.78 and 0.55, respectively.

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Table XXIII.
Series D.

	Stave No. 1	Stave No. 2	Stave No. 3	Stave No. 4	Stave No. 5	Stave No. 6
Total range.....	4.43	2.59	4.67	3.23	3.72	2.20
Average deviation from mean.....	0.99	0.60	1.07	0.62	0.84	0.59
Grand average range in Series D.....						3.55
Grand average deviation form mean Series D.						0.82

Collecting terms from this bulky mass of data, we find:

Table XXIV.

Series	Grand average range between maximum and minimum in six sets of 5 tests each	Grand average deviation from mean, in sets of 5 tests each (Spherical shot tests only)
A.....	2.26	0.69
C.....	2.32	0.73
E.....	2.24	0.64
F.....	3.00	0.84
G.....	3.09 (1.78)[1]	0.90 (0.55)[2]
D.....	3.55[1]	0.82[1]

From the above, it can be seen that while in every large series of results, there are occasional ranges of 3.5, 4 and even 5 per cent. between maximum and minimum, the *ordinary or average range due to structural defects is between 2 and 3 per cent.*, and in a similar way, the ordinary departure of an individual test from the average of its set is about 3/4 of a per cent.

A well marked difference is observable between the first 5 series, composed of materials selected from the kilns with regard to uniformity of heat treatment, and Series D,

[1] Excluding one highly erratic result.

[2] Twelve sets of 10 tests each, instead of six sets of 5 each.

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composed of a commercial shipment diverted from its purpose. The ranges in this series run up to over 5.46 per cent., and in no case fall below 2.20. This is in much closer accord with what is found constantly by engineers who carefully follow up brick deliveries on the street with rattler tests. Some of the material, and often much the largest part, is as good as the bidders' samples, but there is also generally some that is not as good—enough to give fluctuating and irregular tests, which destroy confidence in the test or in the material, according to the affiliation of the tester.

A similar study of the ranges and deviations of the results or the tentative standard comparisons does not disclose anything different, except that one material shows much higher figures. This material is soft and wears excessively in rattling, and as the tests show, is irregular and variable in addition and could not be considered as good or standard brand.

III. THE VARIATION IN ABILITY TO WITHSTAND THE RATTLER TEST DISCLOSED BY DIFFERENT BRANDS OF PAVING BRICKS OF GOOD REPUTATION.

In the foregoing tables (III to IX, inclusive), we have a large amount of data from six standard brands of paving bricks. Owing to variations in the conditions of the rattler test into which it is not necessary to go here, these data are not closely comparable, series to series, and must be set aside for the present purpose. In Tables X and XI we have the same series and four additional ones compared under strictly uniform conditions, in which every detail was most attentively watched. Although Series C and P are represented only by 5 tests each, owing to shortage of material, the other averages represent 10 tests apiece. These results have value for our present purpose. Marshaling the data here, we have:

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Table XXV.

Series	Average of 10 tests	Maximum loss in 10 tests	Minimum loss in 10 tests	Range	Average deviation from mean
A	19.59	20.38	18.72	1.66	0.55
C	24.33[1]	24.97[1]	23.80[1]	1.17[1]	0.36[1]
D	21.47	22.71	19.56	3.16	0.65
E	19.31	20.87	18.08	2.79	0.77
F	18.20–[2]	19.51–[2]	17.30–[2]	2.21–[2]	0.51–[2]
	17.19–[3]	19.27–[3]	15.44–[3]	3.83–[3]	1.18–[3]
G	18.77	19.58	17.90	1.68	0.40
H	27.82	30.47	23.33	7.14	2.31
K	18.92	20.30	17.59	2.71	0.79
M	19.07	20.36	17.24	3.12	0.93
P	16.78[1]	17.40[1]	16.40[1]	1.00[1]	0.28[1]

A scrutiny of the above shows a remarkably satisfactory situation. Of the 10 brands, seven show below 20 per cent. average loss. The other three range in order 21.47, 24.33 and 27.82. In a study of the maxima, we also find that of the seven best materials, three do not reach 20 per cent. and 20.87 per cent. is the highest.

The relation between these figures, and the losses these same bricks would have shown under the old standard of the N. B. B. A. is problematical. The old test varied, as we now know, from a number of causes, chiefly the variable quality and condition of the shot, the lack of uniformity of the staves and heads of the barrels, the lack of uniformity in counting broken brick at the end of the test, the use of either 10 or 11 heavy shots to make up nearest to 75 lbs. of the shot charge, instead of always 10, and insufficiently close regulation of the speed. To compare results obtained in the past by that test is impossible, because we do not know exactly what the above variables were. Only approximations and estimates are now possible.

[1] On 5 tests only.

[2] Original sample, selected from the kiln.

[3] Second sample, chosen from street delivery.

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It is the judgment of the writer that where the old test was done in a careful and skilful manner, with hard shot, stiff staves and closely regulated speed, the new test is distinctly easier than the old—probably by a per cent. Repeated tests demonstrate that the new test is about 2 per cent. easier than the old, if cubes and spheres of the same metal be used and the rattling chamber be the same in each test.

On the other hand, when the old test was executed with soft shot, or a springy, loose-jointed rattler, or with slow speeds (28+) the new test will be from 3 to 6 per cent. higher. It is probable that the average difference over the country as a whole between the new test accurately performed and the old test as it usually has been performed would be at least four per cent. and possibly five per cent higher.

From the preceding it appears, therefore, that the results in Table XXV could safely be marked down by 2 or 3 per cent. in translating into old-test terms. This would mean that seven out of ten of the blocks tested would pass an 18 per cent. standard easily, and 8 would pass at 20 per cent. Only two would have to be rejected.

Of course, it must be borne in mind that these tests generally represent picked material—picked either by Mr. Blair or by the manufacturer. In only one or two cases did the material represent commercial shipments. It is fair to suppose that commercial shipments would show a higher average loss, a higher range and a higher average deviation.

The showing made is good, nevertheless, and it should be useful to both engineers and manufacturers in all parts of the country to see, just at this time, what the brick-makers can do and what the new test will do.

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CONCLUSIONS.

First. The variation in rattler test in well burnt charges of paving brick of one brand, due to position in the kiln, whether top, middle or bottom, has been kept down to between 2 and 3 per cent. in the case of five representative products studied. It would seem that there is no real need of its being allowed to exceed that in well-equipped plants using suitable clays.

Second. The variation in rattler test in uniformly burnt charges of paving bricks of one brand, due to structural causes, is found to run between 2 and 3 per cent. Occasional erratic tests may increase the range to 4 or 5 per cent. This conclusion is drawn from the study of ten brands.

Third. From the foregoing, it follows that in dealing with paving bricks of first-class quality, we must expect a variation of from 3 to 5 per cent. in the output, as measured by rattler losses. In plants where the output is not of first-class quality, due to manufacturing causes, or burning irregularities or unsuitable clay, this margin is likely to be much wider—probably 5 to 8 per cent. in second-quality material and more than that in bad cases.

Fourth. To attempt to judge of the quality of a paving brick by the rattling of a single charge of 10 bricks is entirely improper. With material which, under good conditions, shows an inherent variability within the limits shown above, not less than the average of 5, or better, 10 tests should be insisted upon before ruling out a paving brick because of failure to meet its guarantee or the specified limits.

Fifth. Engineers, in setting the limits of losses in paving bricks tested for any purpose, should invariably insert the word *average* in their specifications. For instance, a properly written clause might say: "When so tested (referring to the method of conducting the test) the *average* loss on rattling 5 (or 10) consecutive charges, chosen as above provided, shall not exceed .... per cent."

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Sixth. If for any reason an engineer is unwilling to abide by the *average* loss of 5 tests, or of all of the tests (exceeding 5) made on the contract in question, and insists upon safeguarding himself by a provision setting a maximum loss above which no single charge may go without throwing out the entire lot of material, this maximum should certainly be very liberal, not less than 5 per cent. above the permissible average in any case.

The writer has here shown that in paving bricks of representative brands, among the best in the country, carefully selected by experts, or by their makers, there will still occur occasional erratic losses of 5 per cent. or more, and while these do not affect the average of large numbers of tests appreciably, they may so occur as to cause the rejection of an excellent material if a hard and fast maximum is insisted upon. In general, the writer believes that a maximum loss provision is not needed by engineers to secure excellent and reliable material, if they have wisely established the limit which the average must not exceed.

Seventh. On the question as to where the average rattler loss of a paving brick should be set to insure a good product, the writer believes that this question is one which should be settled for each locality by itself—it is affected by geographical conditions, freight rates, climatic conditions, traffic conditions in the locality, and by the kind of foundation and mode of laying the street. Obviously, no single standard would be wise or just. If it were made severe enough to be safe for all, it would cause the public to pay more for their streets than necessary in many places, and would put out of business many plants whose product is usefully employed, though not able to meet the drastic specification for important streets in large cities.

Eighth. It has not yet been proven by actual research, so far as the writer is informed, just what the maximum limits of rattler loss may be for a paving brick to make a good street, under normal city conditions on the 40th parallel. Certainly, many bricks which have not been

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able to pass good rattler tests, when well laid, have made excellent streets. Until this relationship between rattler loss and street wear is in some degree established, city engineers should not raise the requirements under the new test higher than at least the average paving brick plant can meet. There exists good ground for the opinion that a mediocre or poor brick, if excellently laid in the street, may surpass the performance of the best bricks, poorly laid. If this should prove to be true, it will not mean the abandonment of the rattler test—it will merely mean a shifting of the limits of acceptance of its verdict.

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